STUDIES in the ELECTROLYSIS of ACETATE SOLUTIONS.

THESIS

for

Degree of Ph.D.

presented by

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C O N T E N T S

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INTRODUCTION.

The investigation of the electrolysis of aqueous acetate solutions has been rendered most difficult on account of the numerous reactions taking place at the anode at the same time. When the conditions of electrolysis, for example current, voltage, acidity, concentration and temperature, are altered, the process at the anode varies. The influence of temperature is well known but has been least investigated.

In the present research are examined the reactions taking place when the temperature of the electrolyte is raised and an attempt is made to eliminate this effect of temperature by a change in the other conditions. An account will first be given of the general reactions which may proceed at the anode. Two theories have emerged to account for these, the "oxidation theory" and the "discharged ion theory", but since the net process is the same, only the former will be considered meantime.

Kolbe (1) first discovered that ethane was synthesised at the anode by the electrolysis of aqueous acetate solutions. This may be represented as follows according to the discharged ion theory:-

$2CH_3COO = C_2H_6 + 2CO_2$ at the anode and

$2H = H_2$ at the cathode (a).

If this were the only reaction taking place

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the volume of ethane would be equal to the volume of hydrogen, i.e. the ratio of ethane to hydrogen would be unity, but this is never the case, the volume of hydrogen always exceeding that of the ethane.

The presence of free oxygen among the gases indicates a second process which is the ordinary Faraday reaction:-

$$2CH_3COO + H_2O = 2CH_3COOH + (O) \quad \text{-------(b)}$$

The oxygen atoms from (b) may unite with each other giving oxygen molecules,

$$O + O = O_2 \quad \text{----------(c)}$$

or they may oxidise completely more of the discharged ions:-

$$2CH_3COO + 7(O) = 4CO_2 + 3H_2O \quad \text{----------(d)}$$

A small amount of ester is also found among the products, arising from the interaction of the discharged ions in another way:-

$$2CH_3COO = CH_3COOCH_3 + CO_2 \quad \text{----------(e)}$$

If the solution is allowed to become alkaline in the course of an electrolysis, or is made alkaline by the addition of carbonate and bicarbonate, then according to Hofer and Moest[2] methyl alcohol is formed:-

$$CH_3COO + OH = CH_3OH + CO_2 \quad \text{----------(f)}$$

Amongst other products may be mentioned unsaturated hydrocarbons, carbon monoxide and Methane.[3]

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In the present series of experiments there is little chance of (f) taking place, acid solutions being used throughout. Difficulty arises in the quantitative estimation of (d) for which the carbon dioxide must be measured accurately.

Influence of Temperature.

The influence of temperature on the electrosynthesis was observed in the earliest of investigations. Bunge [4] observed that the temperature of the electrolyte had a special effect on the nature of the products. He found, on electrolysing an aqueous acetate solution, large amounts of oxygen at 100°C but none at 0°C and very small hydrocarbon yields at 100°C.

T.S.Murray [5], who studied the effect more fully, electrolysed a 20% acetate solution at platinum electrodes with a current of 1.5 amps. Varying the temperature he arrived at the following results:-

Table 1.

Temperature.	0°C	17°	50°	65°	80°	95°
Percentage O_2	0.27	0.31	0.40	0.61	4.17	25.64
C_2H_6/H_2	0.83	0.81	0.69	0.58	0.40	0.12

As Fig.1 shows, the current yield of ethane(a), as measured by the ratio of ethane to hydrogen, fell off /

off gradually with rise in temperature. Diminution became more rapid and finally at 100°C the Kolbe reaction had presumably ceased. The amount of free oxygen (b) increased with the fall in the ratio and at higher temperatures increased rapidly.

Murray then made an oxidation curve. He subtracted the ethane from the hydrogen, half the difference giving the oxygen available for oxidation(A). Subtracting now the percentage of free oxygen he found the oxygen used up in oxidation(B). The ratio B/A then represented the amount of oxygen used in oxidising the electrolyte, as compared with the total oxygen which would have been evolved had no oxidation taken place. His results are given in Table 2(a) and shown by Fig.2(a) :-

Table 2(a).

Temperature	0°C	17°	50°	65°	80°	95°
Oxygen	0.27	0.31	0.40	0.89	4.17	25.64
Ethane	45.23	44.50	40.82	35.78	27.53	8.26
Hydrogen	54.50	55.19	58.78	63.33	68.30	66.10
A	4.63	5.34	8.98	13.77	20.38	28.92
B	4.36	5.03	8.58	12.88	16.21	3.28
B/A	0.94	0.94	0.95	0.93	0.79	0.11

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Fig. 1.

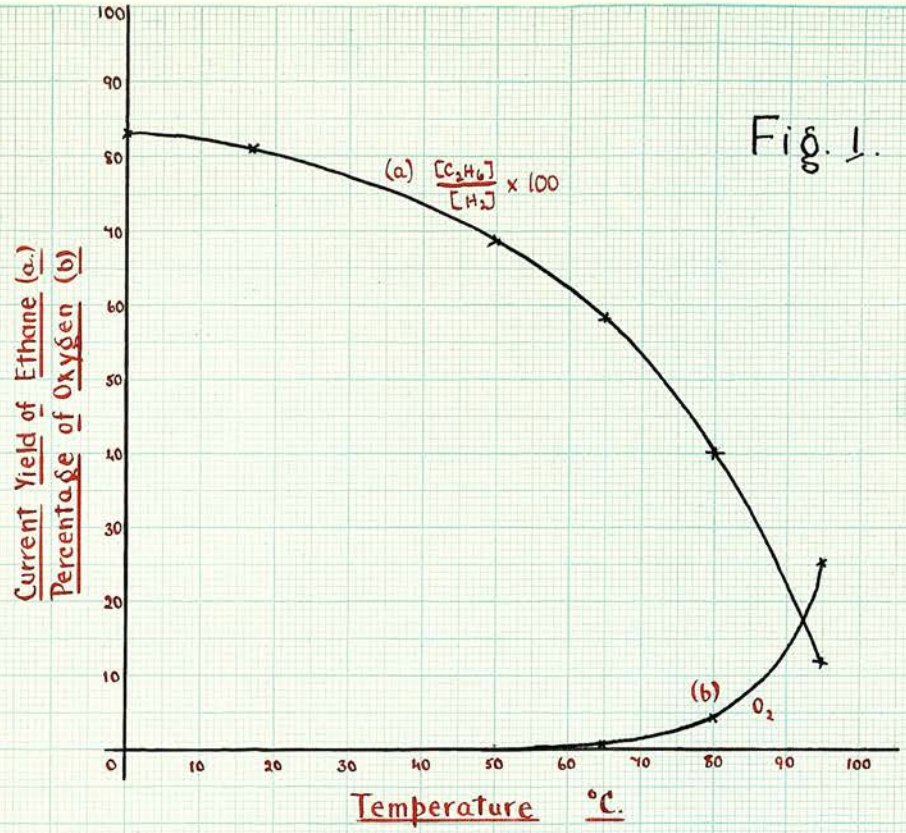
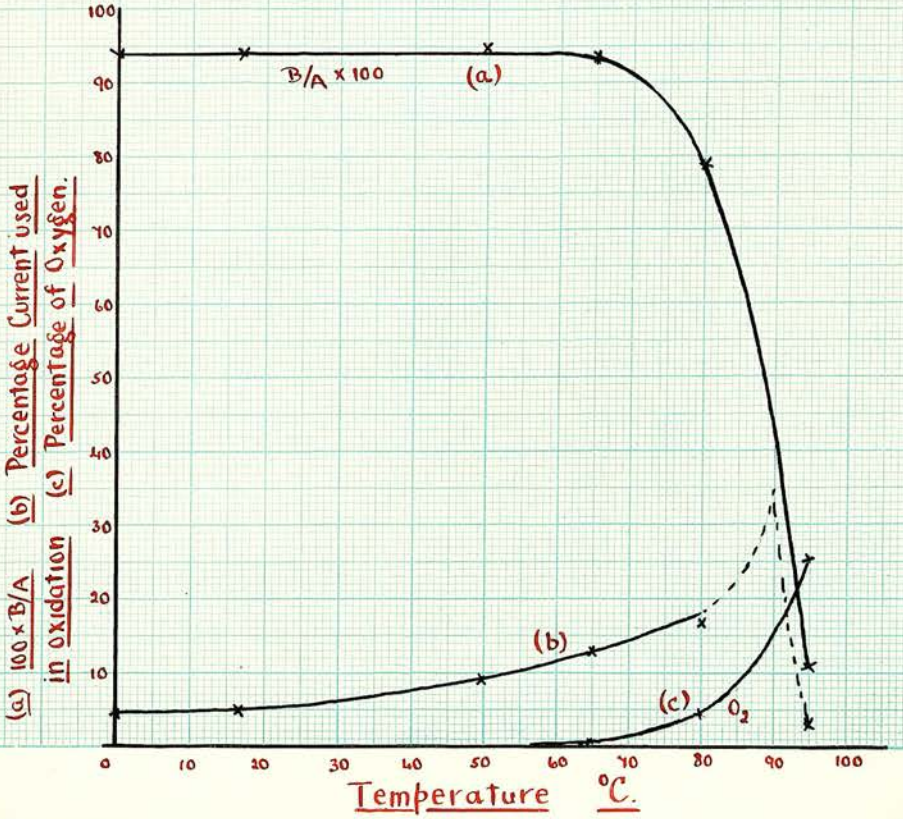

Current Yield of Ethane (a.)
Percentage of Oxygen (b)
(a) $\frac{[C_2H_6]}{[H_2]} \times 100$
(b)
O_2
Temperature °C.

Fig. 2.


(a) 100 × B/A (b) Percentage Current used in oxidation (c) Percentage of Oxygen.
B/A × 100
(a)
(b)
(c)
O_2
Temperature °C.

The interesting part of the curve lies at temperatures between 80° and 95° where a sudden increase in the amount of free oxygen (Fig.2c) is accompanied by a corresponding decrease in the amount of oxidation. This may be seen more clearly by a study of Murray's results from another angle.

The percentage of current used in oxidation purposes is calculated by taking the amount of oxygen used in oxidation (B) as a percentage of half the total hydrogen. The results are then as follows:-

Table 2(b).

Temperature	0°	17°	50°	65°	80°	95°
Oxidation current	4.3	5.0	9.2	13.0	16.5	3.0

The oxidation current increases with rise in temperature to a maximum at the point where the sudden evolution of oxygen takes place, and then falls away. This is shown in Fig.2(b). The key to the problem probably lies with this maximum in the oxidation curve. If this could be removed to lower temperatures, the influence of temperature might be more easily studied.

Murray observed that since change of temperature cannot have any great influence on the electrolysis as far as the concentration of the ions is /

is concerned, reactions other than ethane formation must depend on temperature. It was suggested that water played an important part and that rise in temperature encouraged reactions (b), (c) and (d).

Fairweather and Walker[6] also found the yield of ethane falling off with rise in temperature and complete oxidation on the whole more vigorous at 50°C than at ordinary temperatures. They reasoned that increase in temperature increased the rate of reaction of the discharged ions with water more than the rate of their reaction with each other.

In view of the important part played by temperature in electrosynthesis, it was considered worth while making further investigations in the hopes of obtaining high ethane yields, irrespective of the temperature.

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EXPERIMENTAL.

Materials. Potassium Acetate.

Potassium acetate was prepared from Kahlbaum potassium carbonate and glacial acetic acid which were found to be sufficiently pure for the purpose. The carbonate contained no chloride but perhaps a trace of bicarbonate, for the calculated quantities of these materials usually gave a slightly acid acetate. Potassium carbonate very readily absorbs water so that the presence of water may also have led to the formation of acid acetates.

To the carbonate, placed in a porcelain basin and covered with distilled water, was added gradually and with stirring the calculated quantity of acetic acid. The basin was covered with a clock-glass to prevent loss of material with the evolution of carbon dioxide. The liquid which had collected on the under side of the glass was washed into the basin and the solution transferred to a graduated flask and made up to the mark with distilled water. The solution thus contained a large amount of dissolved carbon dioxide which could easily be removed, if required, by boiling.

To obtain potassium acetate in crystalline form, for use in non-aqueous solvents, the slightly acid solution was evaporated down until a portion placed /

placed on a watch glass deposited crystals on cooling. The main solution was filtered through a hot filter funnel and allowed to cool. The crystals of potassium acetate were then filtered off through a Buchner funnel and left in a vacuum desiccator for several days.

Apparatus for Electrolysis.

The cell, as shown in Fig.3, was made from a thin flat-bottomed test tube, 15cms.by2½cms., fitted with a rubber stopper bored with three holes. One of these carried the outlet tube O which led into a basin of mercury. Through the other two holes passed the platinum electrodes E, each 2 sq.cms. in area. These were sealed into glass tubing and contact was made by mercury. A rubber ring placed round the tube near the top supported the cell on the perforated tray T.

When the stopper was inserted in the cell a twisting effect caused the distance between the electrodes and consequently the internal resistance to vary. T.S.Murray(loc.cit.) states, however, that the results are the same whether resistances are introduced outside or inside the electrolytic cell, i.e. electrolysis is independent of the potential difference between the electrodes, it depends only on current density. A preliminary experiment was performed to verify Murray's statement, details of which will be given later.

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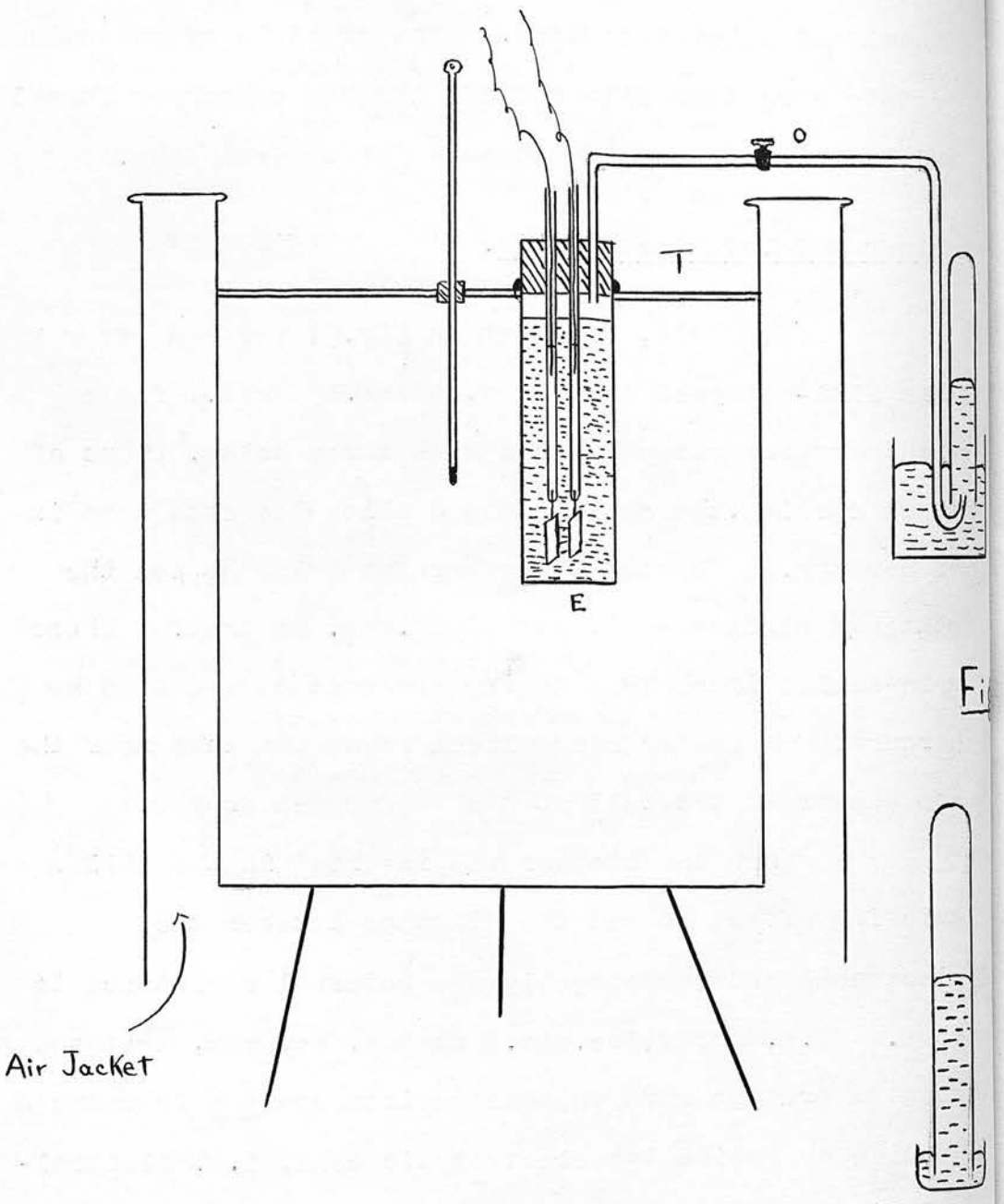
Fig 3.



As rubber absorbs hydrocarbons the stopper was kept wet with solution. Electrolysis never lasted any length of time and the actual time taken to collect the gas was less than two minutes. Absorption of hydrocarbons under these conditions would be small.

The thermostat was so constructed that any desired temperature could be easily reached and maintained for a considerable length of time. It was cylindrical in shape and surrounded with an air-jacket in order that undue loss of heat would be prevented. As the source of heat was an ordinary bunsen the thermostat was supported on a tripod and surrounded with asbestos paper.

With the above arrangement evaporation of water was small up to 60° or 70°C but above this temperature a constant head apparatus was attached. The temperature of the bath remained steady for an hour or two after the flame had been correctly adjusted.

Procedure.

The thermostat was heated up to the required temperature with the water at the level of the perforated tray. The latter carried an accurate thermometer which was placed close to the cell. Owing to the size of the stopper it would have been difficult to introduce another hole to bear the thermometer. If, however, the thermometer were close

to the cell and sufficient time were allowed for the solution within the cell to acquire the temperature of the bath, the reading on the thermometer would be accurate enough for the purpose.

The cell meantime was filled to within a few cms. of the top with the necessary solution, the stopper being inserted with the stopcock open. The distance between the electrodes was usually about 1 cm. The cell was now supported on the tray and adjusted to have the solution level below the water in the thermostat. The outlet tube dipped into the reservoir of mercury. Half an hour to an hour was then allowed for the cell to assume the temperature of the water.

The current was taken from a 100 volt battery of accumulators connected to two large sliding resistances in series and arranged as a potentiometer. An ammeter was placed in the circuit and the voltage across the electrodes measured by a tapping voltmeter.

When the current had passed for a time which varied with the current density, acidity, etc., the gases were collected in test tubes previously filled with mercury and inverted in the reservoir of mercury. Care was taken that none of the solution came over with the gases by keeping the level of the solution in the cell sufficiently low. The air above this was driven out in the preliminary run before the gases were collected.

To /

To transfer the test tube of gas, the end of a fairly wide flat-bottomed tube was cut off and held below the surface of the mercury in the reservoir. The test tube, about two-thirds full of gas, was placed into this, both being lifted out. The gases could be left in this way (Fig.3a) for any length of time or transferred to the gas analysis apparatus.

Analysis of Gases.

The gases, mainly ethane, hydrogen, oxygen and carbon dioxide, were transferred to a Bone-Newitt constant volume gas analysis apparatus.

Preliminary experiments showed only a trace of carbon monoxide and of unsaturated hydrocarbons. Carbon dioxide and oxygen were absorbed, the former measured by the decrease in pressure of the gases after two absorptions with concentrated potash (100 gms. in 100 gms. of water), the latter by the decrease in the pressure of the gases after absorption with alkaline pyrogallol. The pyrogallol solution was stored separately and mixed with the alkali only in the absorption vessel.

The remaining gases, consisting of ethane and hydrogen with possibly nitrogen, were led into the explosion tube with an excess of oxygen. The latter was prepared by heating permanganate in a combustion test /

test tube. The gas was led through potash (to remove permanganate) into a gas reservoir over water. Before mixing with the combustible gases, the oxygen was allowed to stand over potash for several minutes in order to remove any carbon dioxide which had come from the water in the reservoir.

A spark from an induction coil, with a primary voltage of 10 volts, was passed between two platinum wires sealed into the explosion tube. The nature of the explosion depended on the volume of excessive oxygen. With a small excess of oxygen the explosion was violent and a yellowish flame filled the tube immediately. The explosion analysis in this case tended to give higher values for the volume of ethane than were actually present. With a large excess of oxygen the explosion was quiet and a slow blue flame travelled down the length of the tube away from the platinum wires. More consistent results were now obtained in the analysis and conditions were arranged for this type of explosion. The actual volume of oxygen added depended on the volume of ethane present, for the greater the concentration of ethane the greater the amount of oxygen required for combustion.

The volume of ethane was determined from the absorption of the carbon dioxide in the gas left after the explosion. Half the volume of carbon dioxide gave the volume of ethane.

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The volume of hydrogen could be calculated in two ways. Firstly, if the combustible gases consisted only of ethane and hydrogen, it could be found by difference. Secondly, the decrease in the volume of the total gas on explosion was accounted for by the decrease in volume due to the complete oxidation of ethane and of hydrogen. The volume of ethane is known and thus the decrease in volume due to the combustion of ethane. By subtraction, the decrease in volume due to the combustion of the hydrogen is found and hence the volume of the hydrogen itself.

Preliminary experiments showed the hydrogen to be practically the same by both methods. For the present purpose the first method was generally adopted.

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Electrolysis of Acetates in Non-Aqueous Solvents.

Previous Investigations.

Acetic Acid as Solvent.

The electrolysis of acetates in acetic acid with platinum electrodes was observed by Hopfgartner (7), who varied the conditions of concentration, temperature and current, to give products similar to those obtained from aqueous solution.

The ratio of ethane to hydrogen, with a value of 0.85, showed that the Kolbe reaction was the main process. Ethylene and ester were detected but no oxygen was found. The following is a summary of his results:-

Table 3.

Concentration	Temperature	Current	$100 \times C_2H_6/H_2$
2.8%	15°C	0.14amp/dm^2	84.7
2.8	15°C	1.0	87.0
2.8	64°C	0.48.. ..	76.7
2.8	60-66°C	6.0	86.4
8.8	16°C	0.5	90.0
8.8	14-15°C	12.8	92.2
8.8	57-70°C	0.37.. ..	74.1
8.8	66-71°C	48.8	88.7
17.4	43-48°C	0.38.. ..	74.0
17.5	51-53°C	47.7	90.9

For a given solution the current yield of ethane, as measured by the ethane-hydrogen ratio, increases with increase in the current (c,f. aqueous solutions). It also increases with increase in the concentration of the solution but diminishes with rise in temperature. The above table shows that although concentration, temperature and current have the same influence on the electrolysis of acetates in acetic acid as in water, the effect is not nearly so great in acetic acid solutions and a high ethane yield is always obtained.

Methyl Alcohol as Solvent.

Salauze (8) performed a similar set of experiments, electrolysing acetate solutions in methyl alcohol with platinum electrodes. Variation in the temperature of the electrolyte brought about no change in the ethane yield, which is only to be expected with a temperature range of 10° to 30°C. Under similar temperature conditions aqueous solutions give a steady yield.

Salauze obtained yields as high as 98% with methyl alcoholic solutions. This may have been on the high side for his method of gas analysis is open to criticism. Instead of exploding the hydrocarbon and hydrogen residue with excess of oxygen, he absorbed the carbon dioxide and subtracted from the residual gas the voltameter hydrogen, assuming the difference

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to be the volume of ethane. Unsaturated products are not allowed for in his calculations.

Electrolysis of Fused Acetates.

Complications arising from the presence of a solvent are immediately removed by the use of a fused salt. The high temperature of the fused acetate, however, opens up the possibility of side thermal reactions.

Moorhouse (9), who electrolysed a ternary mixture of the acetates of lithium, sodium and potassium, showed recently that ethane was the main product. On account of the lower melting point of a ternary mixture of acetates thermal decomposition was diminished and more consistent results obtained.

His results suggest that the high temperature of fused acetates does not diminish the ethane yield to the same extent as does a much lower temperature with aqueous acetate solutions. The fact that ethane is the chief product apparently shows that the so-called temperature effect is absent. Increase in the temperature brings about a darkening of the melt and thermal decomposition is more liable to take place.

Summary.

The products derived from the electrolysis of acetates in non-aqueous solvents are fewer than from aqueous solution. The main products are, however, the /

the same. Chemical reaction involving the non aqueous solvent does not take place and high ethane yields are obtained at high temperatures. On the other hand, ethane is absent when aqueous solutions are electrolysed at 100°C.

Experimental.

Electrolysis of Acetates in Acetic Acid.

If the decreased current ethane yield is due to the presence of water then it is to be expected that a small amount of water in the solvent will cause an appreciable effect, as other reactions would immediately set in.

Hopfgartner removed the water from the acetic acid with phosphorus pentoxide. The ethane yield diminished with rise in the temperature of the solution but one cannot be certain that all moisture had been removed. In the present experiment the acetate was refluxed for several hours with glacial acetic acid and a slight excess of acetic anhydride.

The dried potassium acetate, made from potassium carbonate and acetic acid as above, was just on the acid side of neutral. 10 gms. of acetate together with 95 to 100 gms. of glacial acetic acid and 5 gms. of acetic anhydride were refluxed together and /

and some of the solution poured into the cell described above, time being allowed for the solution to acquire the temperature of the thermostat.

As acetic acid conducts electricity poorly a voltage of 90 volts was required for 0.5amp. to pass between the platinum electrodes.

The gases were contaminated with acetic acid vapour but this was removed along with the carbon dioxide when the absorption was made with potash. Oxygen was not found among the gases. The results of the experiment are as follows:-

Current Density = 0.25 amp.per cm.^{2}

Table 4.

Temperature	13.6°	13.6°	90.0°	90.0°
$100xC_2H_6/H_2$	96.0	96.4	92.3	96.0

A comparison of the above results with those of Hopfgartner indicates that the conditions of electrolysis were not the same. No marked change in the current ethane yield is observed in the above experiment where the temperature rise is considerably greater than in the corresponding experiment of Hopfgartner.

Gold Electrodes.

Salauze (8) electrolysed acetates in methyl alcoholic solution with various anode materials. The nature /

nature of the anode, provided it was not attacked, was found to have much less influence than in aqueous solution. The gold was attacked.

The electrolysis of a solution of anhydrous sodium acetate in glacial acetic acid at a gold anode was found by Fairweather and Walker[6] to give an ethane-hydrogen ratio of 0.77. Synthesis therefore takes place readily at a gold anode in acetic acid.

Moorhouse[9] obtained poor ethane yields electrolysing fused acetates at gold electrodes. This he accounted for on the basis of a trace of water being present in the melt.

Electrolysis of 10% Acetate in Acetic Acid.

Some of the same solution as was used in the corresponding experiment with platinum electrodes was electrolysed at a gold anode. The latter consisted of gold wire twisted into a flat spiral and of such a length as to give approximately the same area as the platinum electrodes used above. Electrolysis was performed at different temperatures with the following results:- Oxygen was absent. Current Density = 0.25amp./cm.^{2}

Table5.

Temperature	14°	64°	69.6°	93°	93°
$100xC_2H_6/H_2$	95.3	94.4	94.2	93.0	93.0

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As the above table indicates, the ratio of ethane to hydrogen does not alter appreciably with rise in the temperature of the electrolyte.

Carbon Electrodes.

Carbon arc electrodes were substituted in place of the gold electrodes and the experiment repeated with the same solution and current density. High ethane yields were again obtained as the following table shows:-

Table 6.

Temperature	16°C	90°C
$100xC_2H_6/H_2$	88.6	77.8

Rise in temperature does bring about a diminution in the current ethane yield, which may be accounted for by the presence of water. The usual care was taken in the preparation of water-free acetic acid but owing to the high adsorption powers of carbon, water may have been present in sufficient quantity to cause the decreased yield.

Electrolysis with the Addition of Water.

Platinised Platinum.

Electrolysing acidified acetates in methyl alcoholic solution at a platinised platinum anode, Fairweather /

Fairweather and Walker (loc.cit.) added different amounts of water and found a diminution in the ethane yield. The solution contained 4.9 gms. of potassium acetate and 1.52 gms. of acetic acid in 100c.c. of methyl alcohol. The anode was o.165 sq.cms. in area and the current 25 milliamp. :-

Table 7.

CH_3OH(c.c.)	100	95	90	80	0
H_2O (c.c.)	0	5	10	20	100
C_2H_6/H_2	0.71	0.58	0.22	0	0

A trace of water is sufficient to cause a distinct fall in the yield.

Bright Platinum.

Bright platinum electrodes favour high current ethane yields even if water is present. Diminution in such a case only takes place when the temperature of the solution is raised.

Gold Electrodes.

The diminution in the ethane yield is even more rapid in the case of a gold anode. An experiment similar to that of Fairweather and Walker whose results are given above, was performed. Acetic acid was used as /

as solvent. The solution in each case contained 10 g. of potassium acetate per 100 gms. of solvent. The same current density of 0.325 amp./cm.^{2} was employed throughout and electrolysis was conducted at room temperature.

10% acetate in 100% acetic acid. -- Gold Anode.

The result of this experiment has already been indicated in Table 5. 95% of the current was given to ethane formation and since unsaturated hydrocarbons were present only in trace the residual 5% must have been used in oxidation. It is noteworthy that although darkening of the gold took place no disintegration was observed.

10% acetate in 99% acetic acid.

A sample of acetic acid containing 1% of water by weight was used as solvent. The gold again darkened in colour during electrolysis but disintegration was only made visible by a pale yellow colouring of the solution.

On analysis the gases evolved gave the following percentage composition:-

Oxygen	0.59
Ethane	39.26
Hydrogen	60.15

The distribution of current in the various reactions is then as follows:-

Kolbe /

Kolbe Reaction	100 x C_2H_6/H_2	65.3
Faraday ..	100 x $O_2/\frac{1}{2}H_2$	1.9
Oxidation	by difference	32.8

10% acetate in 90% acetic acid.

The gold disintegrated with a solvent containing 10% of water. The gases were analysed and the current was found to be distributed as follows in the various reactions:-

Kolbe Reaction	100 x C_2H_6/H_2	1.64
Faraday ,.	100 x $O_2/\frac{1}{2}H_2$	58.5
Oxidation	by difference	39.9

10% acetate in water.

With water as solvent no ethane was formed, the gases being composed mainly of oxygen and hydrogen. 85% or more of the current was given to the Faraday reaction.

Discussion.

It has been shown that the nature of the anode and temperature have little effect on the products arising from the electrolysis of acetates in non aqueous solvents. This is due to the inability of the discharged ions to react with the solvent. Immediately water is added reaction takes place with the discharged ions and ethane formation is inhibited. This is more pronounced /

pronounced at higher temperatures. The effect due to anode material is also dependent on the amount of water in the solvent as has been shown by the previous investigators and by the above experiments with gold electrodes, the results of which are best seen from the following summary:-

Table 8.

Composition of Solvent	CH_3COOH	100g.	99g.	90g.	0g.
	H_2O	0g.	1g.	10g.	100g.
Current Yield	Kolbe	95.0	65.3	1.64	0
	Faraday	0	1.9	58.5	85
	Oxidation	5.0	32.8	39.9	15

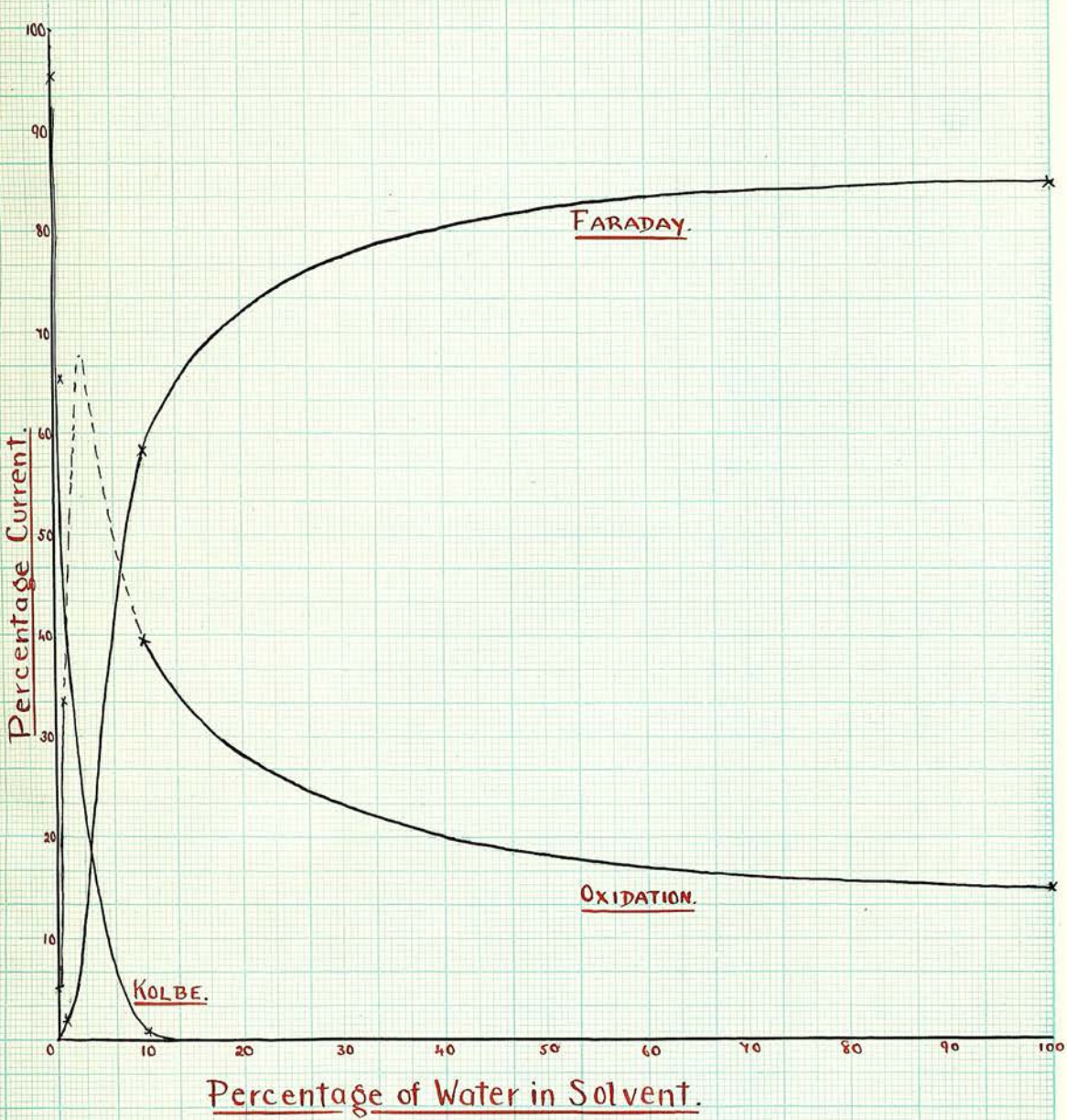
These are shown diagrammatically in Fig.4 where the percentage of current distributed in each of the three reactions is plotted against the percentage of water in the solvent.

With the addition of water the current yield of ethane falls off rapidly. The free oxygen yield increases rapidly at first and then steadily but oxidation increases rapidly to a maximum at the point where the ethane yield has fallen to zero, and then falls steadily.

Reference will be made later to this type of curve.

Electrolysis /

Fig. 4.


Percentage Current.
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
FARADAY.
OXIDATION.
KOLBE.
Percentage of Water in Solvent.

Electrolysis of Aqueous Acetates at various Temperatures.

As far as the influence of temperature on the electrolysis of aqueous acetates is concerned, interest lies only in the use of bright platinum as anode material for this gives high ethane yields at ordinary temperatures. Platinised platinum and gold give no synthesis and carbon only a moderate yield. Unless otherwise stated it will be assumed in the following experiments that bright platinum electrodes were employed.

Electrolysis of 5% acetate solution.

By a 5% solution is meant 5 gms. of potassium acetate in 100c.c. of solution. This solution was prepared as above (page 7) and made slightly acid so that, after the electrolysis had gone for some time, the gases could be collected when the solution was neutral or just on the acid side.

Current Density = 0.24 amp. per sq.cm.

A preliminary run was made for half an hour to allow the gases evolved to reach equilibrium. The gases were then collected and analysed. The results of the analysis are shown in Table 9 which gives the percentage composition and the ratio of ethane to hydrogen. The latter is subtracted from 100 and the difference, which is the current used in both /

both the Faraday and oxidation reactions, is then plotted against temperature as in Fig. 5(a).

From (A), the amount of oxygen available for oxidation purposes, i.e. half the difference between the percentage of ethane and the percentage of hydrogen, is subtracted the percentage of free oxygen, the difference giving the oxygen used in oxidation (B). The ratio of 100 x B to A is then plotted against temperature as in FIG.5 (d).

The percentage of current used in the Faraday reaction is one hundred times the ratio of free oxygen to half the total hydrogen. The variation of this ratio with temperature is shown by Fig. 5 (b).

Finally, the percentage of current employed in oxidation may be calculated by subtracting the current used in free oxygen formation from the current used for purposes other than ethane formation, or by multiplying the ratio, oxygen disappeared (B) to half the total hydrogen, by 100. The variation of this current with temperature is given by the curve 5 (c).

Table /

Table 9.

Temperature Voltage	13°C 6.6	37.3° 5.3	60.3° 4.5	64° 4.1	74.5° 3.7	92.5° 3.35	Curve
O_2	0.4	0.7	6.1	12.4	27.6	30.0	
C_2H_6	46.67	42.17	16.68	6.11	1.90	0.56	
H_2	52.93	57.13	77.22	81.49	70.50	69.44	
100 x C_2H_6/H_2	88.2	73.8	21.6	7.5	2.7	0.8	
Oxidation and Faraday Current	11.8	26.2	78.4	92.5	97.3	99.2	(a)
A Available Oxygen	3.13	7.48	30.27	37.69	34.30	34.44	
B Oxygen disappeared	2.73	6.78	24.17	25.29	6.70	4.44	
100 x B/A	87.2	90.6	80.0	67.1	19.5	12.9	(d)
Faraday Current	1.5	2.5	15.8	30.4	78.3	86.4	(b)
Oxidation Current	10.3	23.7	62.6	62.1	19.0	12.8	(c)

It is evident that (a) is the sum of (b) and (c) while (d) is the ratio of (c) to (a) multiplied by 100. The oxidation curve (c), showing a maximum, is approximately the curve obtained by the intersection of (a) and (d), below the point of intersection.

If the earlier part of the oxidation curve (c) up to the maximum were to coincide exactly with (a), all /

all the available oxygen would then be used in oxidation and no free oxygen would appear. Curve (d) in that case would lie along the 100% mark instead of the 90% mark. As (c) almost coincides with (d) beyond the maximum in the oxidation curve, the presence of ethane is still indicated. If ethane were absent (c) and (d) would coincide exactly.

Distribution of Current among the various Reactions.

The course of events as the temperature of the electrolyte is raised is best seen from a study of the distribution of current. In Fig. 6 is plotted the percentage current used (a) in ethane formation, (b) in oxidation and (c) in free oxygen formation, the processes involved coming under these three headings.

The current yield of ethane falls off slowly at first while the current used in oxidation increases slowly. Diminution of the ethane yield becomes more rapid and a corresponding increase takes place in the amount of oxidation until a maximum in the oxidation curve is reached. At this temperature the ethane yield has fallen off almost to zero but oxygen has made its appearance.

When the temperature of the electrolyte is raised further, the oxygen yield increases, oxidation decreases and ethane can just be detected. At higher temperatures, no ethane is present, very little oxidation takes /

Fig. 5.

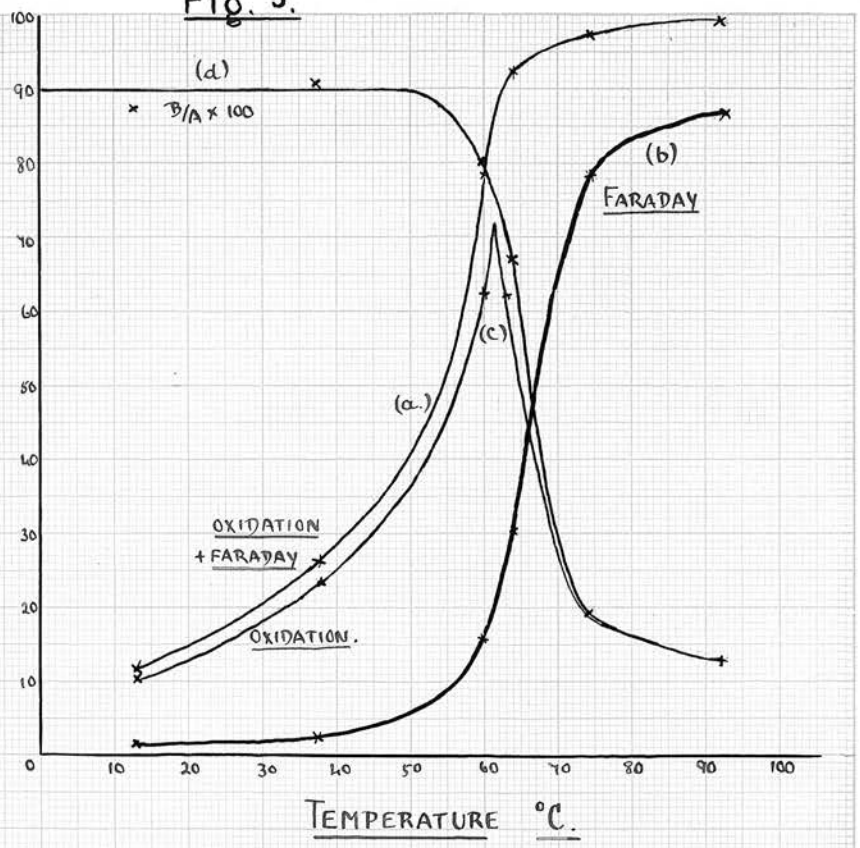
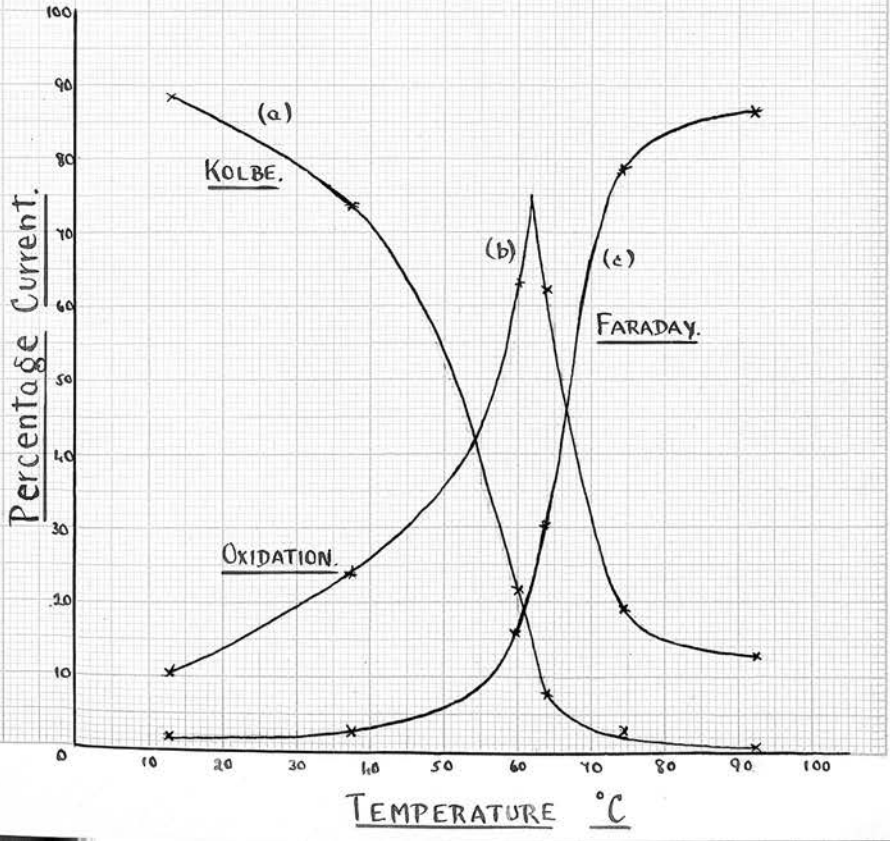

(d)
× B/A × 100
(b)
FARADAY
(c)
(a.)
OXIDATION
+ FARADAY
OXIDATION.
TEMPERATURE °C.

Fig. 6.


Percentage Current.
(a)
KOLBE.
(b)
(c)
FARADAY.
OXIDATION.
TEMPERATURE °C

takes place while most of the current is utilised in the Faraday reaction. Thus at low temperatures the Kolbe reaction is the main process, at higher temperatures oxidation and at higher temperatures still the Faraday reaction.

Electrolysis of 10% acetate solution.

A 10% solution of potassium acetate in water, slightly acid, was prepared as above and electrolysed as in the case of the 5% solution. The results were calculated in a similar way and shown diagrammatically in Fig. 7 :-

Current Density = 0.24 amps. per sq. cm.

Table 10. /

Table 10.

Temperature Voltage	13°C 5.5	36.7° 4.25	62° 3.7	73.3° 3.4	93° 3.0	Curve
O_2	0.31	0.51	1.51	20.0	28.2	
C_2H_6	47.41	45.43	37.62	6.4	0.74	
H_2	52.28	54.06	60.87	73.6	71.06	
100 x C_2H_6/H_2	90.6	84.0	61.8	8.7	1.0	
Oxidation and Faraday Current	9.4	16.0	38.2	91.3	99.0	(a)
A Available Oxygen	2.44	4.32	11.63	33.60	35.16	
B Oxygen disappeared	2.13	3.81	10.12	13.60	6.96	
100 x B/A	87.0	88.0	87.0	40.0	20.0	(d)
Faraday Current	1.19	1.89	5.0	54.3	79.4	(b)
Oxidation Current	8.2	14.1	33.2	37.0	19.6	(c)

The curves obtained are similar to those from the 5% solution. The fall in the ethane yield takes place at a higher temperature and the maximum in the oxidation curve has been displaced to a higher temperature.

Electrolysis /

Electrolysis of a 20% acetate solution.

The above experiment was repeated with a 20% solution of potassium acetate. The same current density of 0.24 amps. per sq. cm. was employed. Results as follows:-

Table 11.

Temperature Voltage	14.4°C 4.25	46.0° 3.5	74.2° 3.1	95° 2.5	Curve
O_2 C_2H_6 H_2	0.3 47.53 52.17	0.4 44.45 55.15	2.0 25.35 72.65	22.4 1.11 76.49	
100 x C_2H_6/H_2	91.1	80.6	34.9	1.45	
Oxidation and Faraday Current	8.9	19.4	65.1	98.55	(a)
A Available Oxygen B Oxygen disappeared	2.32 2.02	5.35 4.95	23.65 21.65	37.69 15.29	
100 x B/A	87.1	92.5	91.6	40.6	(d)
Faraday Current	1.2	1.45	5.5	58.56	(b)
Oxidation Current	7.7	18.0	59.6	40.0	(c)

As Fig. 8 shows, the maximum in the oxidation curve has been further displaced to higher temperatures.

Electrolysis /

Fig. 7.

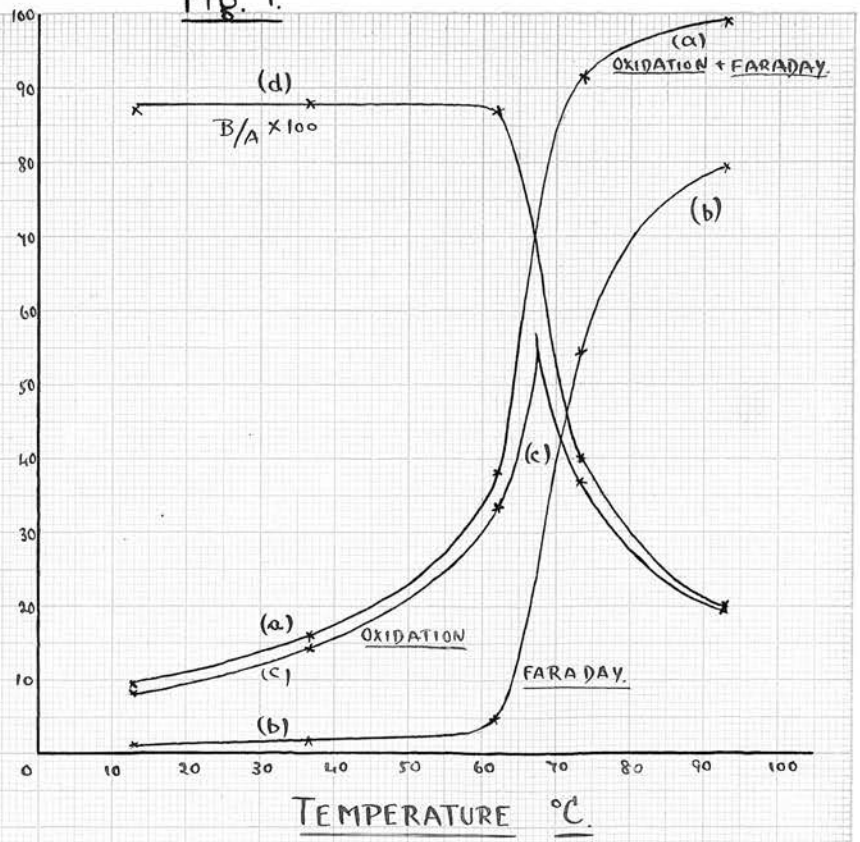
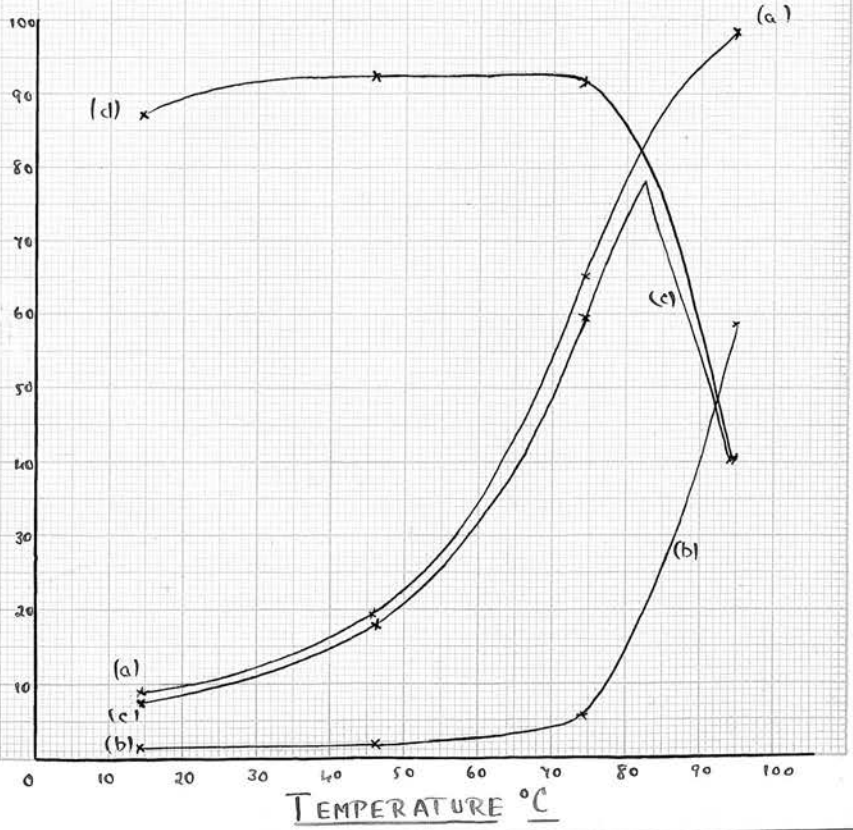

(a)
OXIDATION + FARADAY
(d)
B/A × 100
(b)
(c)
(a)
OXIDATION
(c)
FARADAY.
(b)
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
TEMPERATURE °C.

Fig. 8.


(a)
(d)
(c)
(b)
(a)
(c)
(b)
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
TEMPERATURE °C

Electrolysis of the same solution with a higher Current.

The 20% aqueous acetate solution was again electrolysed. The current density was increased to 1.25 amps. per sq. cm. The results of the analysis of the gas are given in Table 12 and shown in Fig. 9:-

Table 12.

Temperature	11°C	45°	79.5°	92°	Curve.
O_2	0.2	0.35	0.8	1.4	
C_2H_6	47.4	46.67	43.47	42.05	
H_2	52.4	52.98	55.73	56.55	
100 x C_2H_6/H_2	90.5	88.1	78.0	74.34	
A Available Oxygen	2.5	3.16	6.13	7.25	
B Oxygen disappeared	2.3	2.81	5.33	5.85	
100 x B/A	91.0	89.0	87.0	80.7	(d)
Oxidation and Faraday Current	9.5	11.9	22.0	25.6	(a)
Faraday Current	0.7	1.3	2.9	4.9	(b)
Oxidation Current	8.8	10.6	19.1	20.7	(c)

The ethane yield falls off very slowly. This means an almost steady value for the current used in /

Fig. 9.

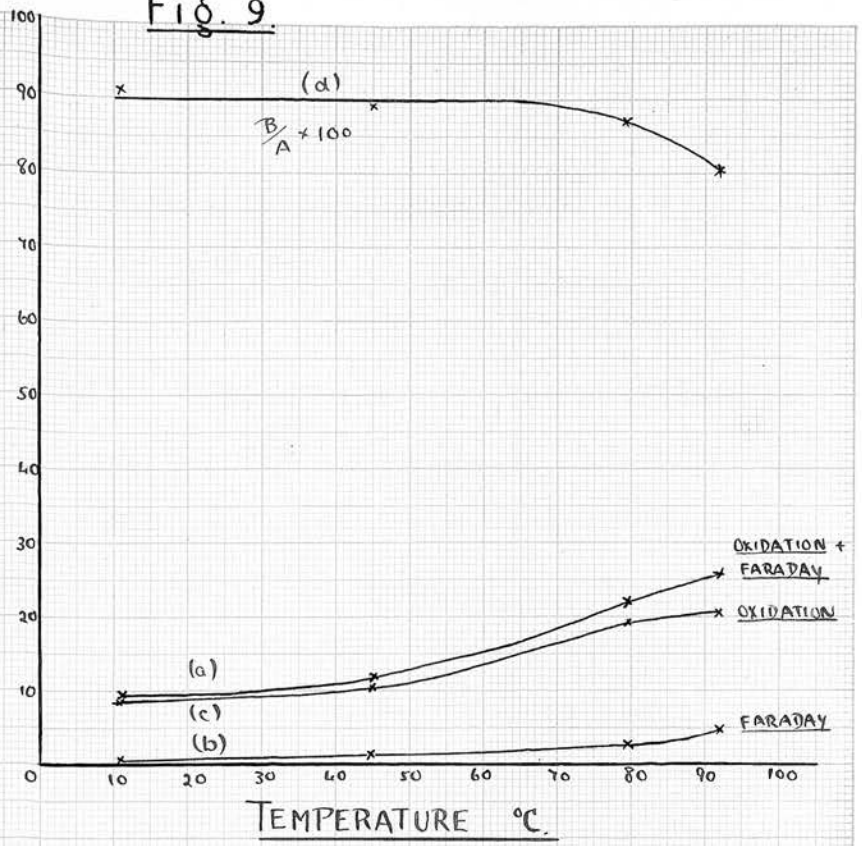
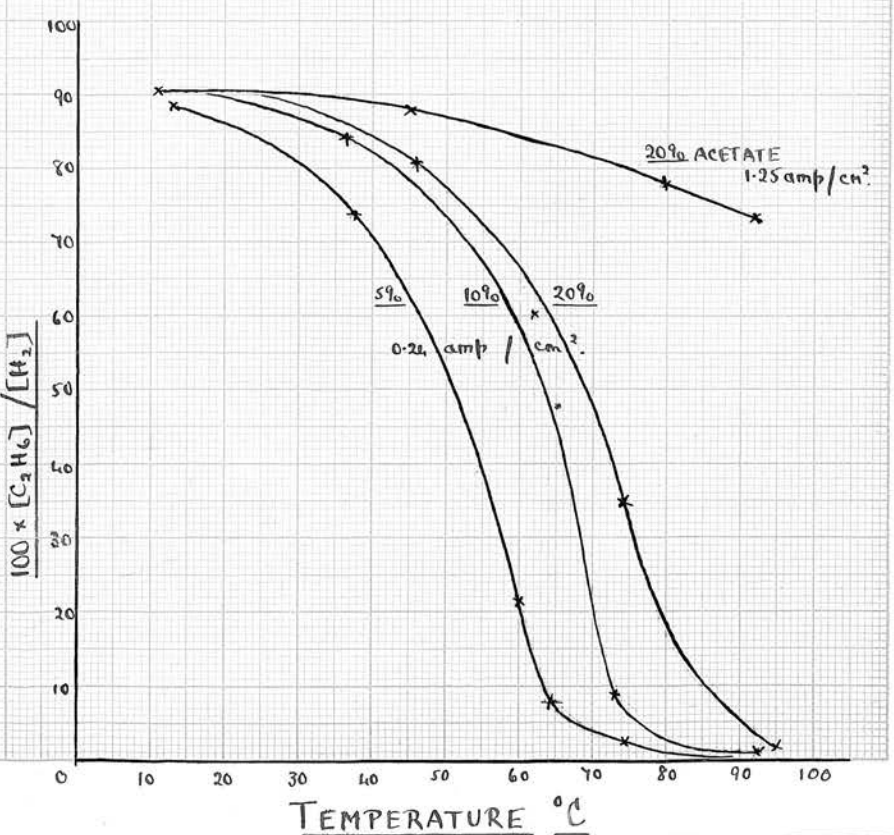

(a)
B/A × 100
OXIDATION + FARADAY
OXIDATION
FARADAY
(a)
(c)
(b)
TEMPERATURE °C.

Fig. 10.


20% ACETATE 1·25 amp/cm²
5%
10%
20%
0·2A amp / cm².
100 × [C₂H₆] / [H₂]
TEMPERATURE °C

in the oxidation and Faraday reactions. No maximum appears in the oxidation curve and free oxygen does not appear freely even at high temperatures.

The above experiments illustrate that if an increase is made in the concentration of the solution or in the current density, the influence of temperature is not so marked. Fig. 10 shows the ethane:hydrogen curves for the 5%, 10% and 20% acetate solutions.

In the next set of experiments an attempt has been made to increase the ethane yield at high temperatures by increasing the concentration of the solutions and the current density. Electrolysis in each case was performed at 90°C.

Electrolysis of Acetate Solutions in water at 90°C.

In order to keep the conditions of electrolysis as constant as possible, the acidity of the solution had to be the same in each case when a sample of the gas was collected. The different solutions, saturated with ethane, were made up having the same acidity and the same volume (20c.c.) was used in each electrolysis. To displace the air from the cell, the current was allowed to run for one hour at 0.25 amp. per sq. cm., or half an hour when the current density was 0.5 amp. per sq. cm. and so on, before samples of the gas were collected.

Electrolysis of 10% Aqueous Acetate at 90°C.

10% aqueous acetate was made up containing 5.0 gms. of acetic acid per 100c.c. of solution and electrolysed. The following are the results of the gas analysis:-

Table 13.

Current Density	0.25amp/cm^2	0.5amp/cm^2	1.0amp/cm^2
Voltage across Electrodes	3.0	4.3	5.8
O_2	15.5	5.1	3.9
C_2H_6	3.25	17.9	27.08
H_2	81.25	77.0	69.02
100 x C_2H_6/H_2	4.0	23.2	39.3

The variation of the current yield of ethane with current density is illustrated by Fig. 11a. The type of curve is similar to that obtained by Murray (loc.cit.) who electrolysed an acetate solution at ordinary temperatures varying the current density.

The lower ethane yield obtained at lower current densities is due to the fact that the voltages across the electrodes are not far removed from the decomposition voltage of acetates.

Electrolysis /

Electrolysis of 20% Aqueous Acetate at 90°C.

100c.c. of the solution again contained 5.0 gms. of acetic acid. The gases evolved on electrolysis gave the following analysis:-

Current Densities are in amps./cm^2.

Table 14.

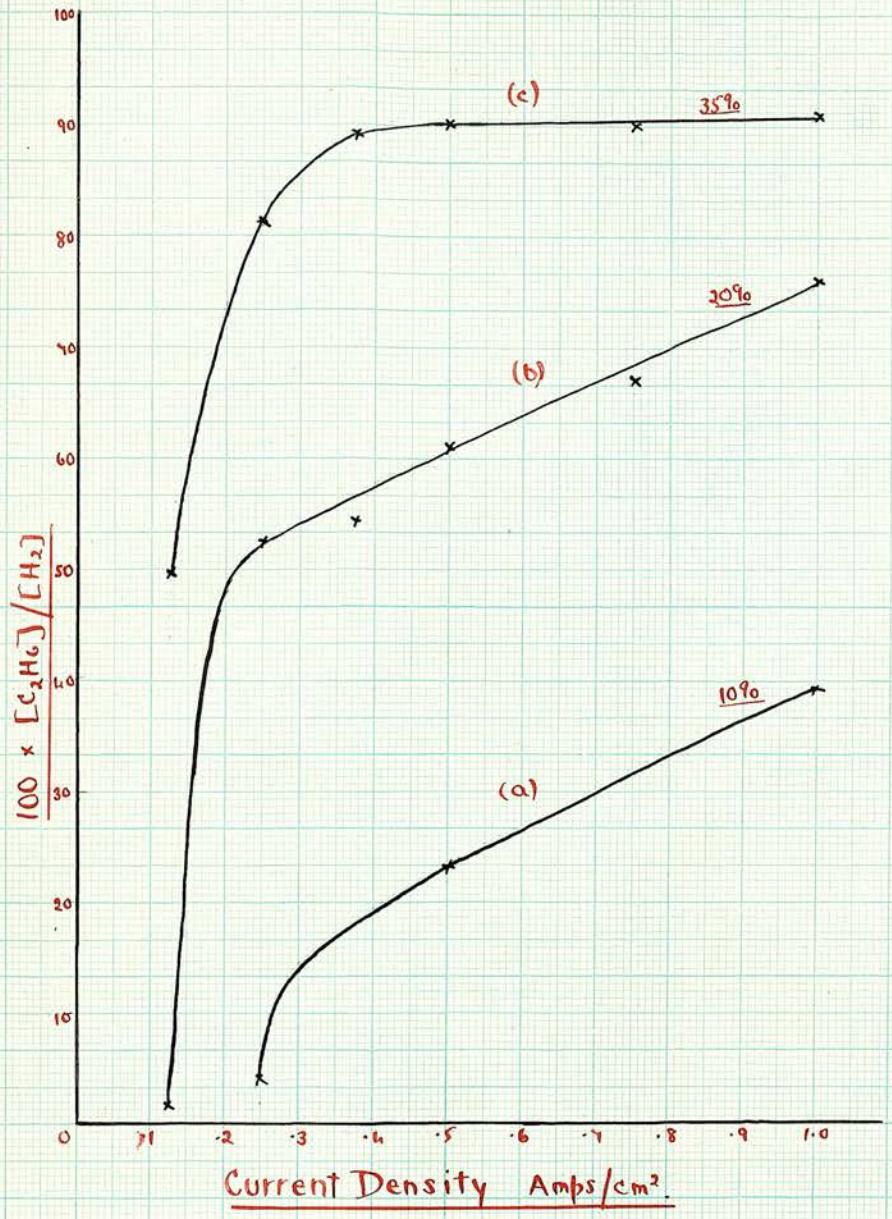
Current Density	0.125	0.25	0.375	0.5	0.75	1.0
Voltage across Electrodes	2.7	3.6	3.8	4.4	5.0	5.9
O_2	19.6	1.1	1.9	2.2	2.6	1.3
C_2H_6	1.96	34.06	34.72	37.2	39.2	42.6
H_2	78.44	64.84	63.38	60.6	58.2	56.1
100 x C_2H_6/H_2	2.5	52.5	54.8	61.3	67.3	76.0

The variation of the ethane:hydrogen ratio with current density is shown by Fig.11b. Provided the voltage across the electrodes is above the decomposition voltage, the main process once again becomes the Kolbe reaction. This means that a good ethane yield may be obtained at high temperatures with an aqueous solution of high enough concentration. The oxygen yield was small except at low current densities.

Electrolysis of 35% Aqueous Acetate at 90°C.

The 35% aqueous solution was decidedly viscous /

Fig. 11.


100 × [C2H6]/[H2]
100
90
80
70
60
50
40
30
20
10
0
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0
(c)
35%
(b)
20%
(a)
10%
Current Density Amps/cm².

viscous and the gases took longer to escape. The conditions were now more like those of a solution of an acetate in a non aqueous solvent.

As the gases from the electrolysis of this solution only gave a faint coloration with alkaline pyrogallol, oxygen was not measured. The ethane to hydrogen ratios only are given in the following table:-

Table 15.

Current Density	0.125	0.25	0.375	0.5	0.75	1.0
Voltage across Electrodes	3.2	3.9	4.3	4.8	5.2	6.2
100 x C_2H_6/H_2	49.84	81.4	89.2	90.6	90.0	91.7

The variation of the current ethane yield with current density is shown by Fig. 11c. The yields obtained were about the same as with dilute aqueous solutions at ordinary temperatures.

DISCUSSION.

Discharged Ion Theory.

The reactions have been considered so far in the light of the discharged ion mechanism. The theory was first advanced by Crum Brown and Walker (10) and has been supported by Murray, (5) Hamonet, (11) Preuner and Ludlam (12) and by Fairweather and Walker. (6)

Since /

Since the electrolysis of aqueous acetates depends on the nature of the anode, the reaction may be assumed to be to a large extent catalytic.

At low temperatures the rate of reaction between the discharged ions,

$2CH_3COO = C_2H_6 + 2CO_2$ ----------(a),

is greater than the rate of reaction between the discharged ions and water,

$2CH_3COO + H_2O = 2CH_3COOH + (O)$ ---(b).

Ethane is thus the main product. The rate of complete oxidation of the discharged ions by oxygen atoms arising from (b),

$2CH_3COO + 7(O) = 4CO_2 + 3H_2O$ ------(c),

being greater than the rate of interaction of the oxygen atoms,

$O + O = O_2$ ----------(d),

only a small amount of free oxygen appears at ordinary temperatures.

As the temperature is raised the rate of reaction (b) at the surface of the platinum is increased and the increased number of oxygen atoms oxidises completely more of the discharged ions. As there is a limit to the number of discharged ions, depending on the current density, fewer discharged ions will be left to form ethane. The ethane yield therefore drops and oxidation increases. The rate of oxygen gas formation /

formation (d) is still small.

The ethane yield falls at first slowly then more rapidly with rise in the temperature of the electrolyte, until finally a temperature is reached when the number of oxygen atoms from (b) is more than sufficient to oxidise the remaining discharged ions. The ethane yield is now almost zero. Although the union of oxygen atoms is slow compared with other oxidation processes involving the oxygen atom, yet all the remaining discharged ions have been used up and the excess of oxygen atoms can only react with each other according to (d). Oxygen thus appears.

With a further rise of temperature reaction (b) is still more catalysed, fewer discharged ions being left for oxidation. Oxidation decreases and free oxygen increases. A maximum therefore appears in the oxidation curve and oxidation continues to decrease at the expense of the increasing oxygen yield.

The so-called "Temperature Effect" is due essentially to the presence of the water. The less water present the better the yield of ethane at high temperatures. On the surface of the platinum there are water molecules, acetate ions and discharged ions. If the current density is kept constant the number of discharged ions is constant and increase in the concentration of the solution brings about a decrease in /

in the number of water molecules at the anode as compared with the number of discharged ions. Reactions (b), (c) and (d), due to the water, do not take place to the same extent and higher ethane yields are obtained at high temperatures.

An increase in the current density provides an increase in the number of discharged ions at the surface of the anode. Irrespective of whether the number of water molecules at the anode thereby decreases or remains the same, the number of water molecules per discharged ion must necessarily diminish. Hence the reactions due to the presence of water are less prominent and higher ethane yields are obtained.

Oxidation Theory.

So far no mention has been made of the "Oxidation Theory" which was the original one advanced by Kolbe. Ethane according to this theory is derived from a secondary reaction:-

$$2CH_3COOH + (O) = C_2H_6 + 2CO_2 + H_2O. \quad \text{----(e)}$$

Acetic acid is assumed to be present and the first process is the Faraday reaction. Complete oxidation according to this theory would proceed as follows:-

$$CH_3COOH + 4(O) = 2CO_2 + 2H_2O \quad \text{---------(f)}$$

(4)

This theory has been supported by Bunge, Schall /

Schall,[13] Gibson,[14] Robertson,[15] Foerster and Piguet[16] and by Fichter.[17]

It is highly improbable that complete oxidation will take place as in (f). It will be recalled that acetate solutions acidified with acetic acid were used and when the gases had been collected the solution was still on the acid side of neutral. Hence at temperatures beyond that at which the maximum in the oxidation curve appeared, acetic acid molecules and oxygen atoms did exist together but oxidation decreased. If complete oxidation were to take place according to the "Oxidation Theory" there should be no maximum in the oxidation curve in the case of acidified solutions, for oxidation could still proceed.

The only conclusion to be drawn is that oxidation cannot take place in the light of the "Oxidation Theory."

Peroxide Theory.

There still exists the possibility of the reactions proceeding through the intermediate formation of a peroxide. Fichter[17] especially supported this view. There is little against this theory except that attempts made to isolate the peroxide have not been successful.

Matsuda[18] has recently observed from experiments /

experiments on hydrogen ion concentration that the process at the anode, in the electrolysis of aqueous acetate solutions, is best explained by the assumption that acetyl peroxide is formed as an intermediate product. He attributes the presence of hydrogen peroxide to the hydrolysis of acetyl peroxide. As electrolysis proceeds and the solution becomes more alkaline, the concentration of the hydrogen peroxide increases to a maximum and then decreases. This he observed to be due to the instability of the peroxide in alkaline solution, although his results show that the maximum yield was obtained long after the solution had turned alkaline.

He gives no evidence in his experiments of the existence of acetyl peroxide nor does he prove definitely that hydrogen peroxide is the substance which oxidises the potassium iodide. Besides, the presence of hydrogen peroxide may just as readily be accounted for on the basis of the discharged ion mechanism or even by oxidation of acetic acid.

The conclusions arrived at by Walker (19) still hold. He examined the properties of acetyl peroxide and showed that the intermediate formation of this substance during electrolysis was most improbable and certainly not essential. Besides, the end result is the same whether there is an intermediate peroxide or not.

Oxidation Current.

For the sake of simplicity in the foregoing experiments, it was assumed that three main reactions took place, namely, the Kolbe reaction, the Faraday reaction and oxidation processes involving the residual current. Under'oxidation'processes come complete oxidation, ester formation and methyl alcohol formation, although 'oxidation' is not a necessity.

In the quantitative determination of reactions taking place at the anode difficulty arises in the estimation of the carbon dioxide. Even with an acetate solution saturated with the gas, as electrolysis proceeds the solution becomes more alkaline and absorbs more gas with the formation of carbonate or bicarbonate. This difficulty may be avoided by the use of a solution sufficiently acid to remain so during electrolysis and, when the gases are collected, to be just on the acid side.

With an acid solution of acetate saturated with carbon dioxide, the amount of carbon dioxide evolved should be sufficient, although the solution as a whole is becoming less acid, to keep it saturated. As the time taken to collect the gas is short, the amount of carbon dioxide coming over should be as near as may be the amount given off in the electrolysis.

Preliminary /

Preliminary experiments were carried out at ordinary temperatures with bright platinum electrodes.

Oxidation Current at Ordinary Temperatures.

A 10% potassium acetate solution, containing 7½% of acetic acid, was saturated with carbon dioxide and electrolysed with a current density of 0.5amp./cm.^{2} Electrolysis was allowed to proceed for a quarter of an hour before a sample of the gas was taken. Samples were then collected at the end of every 15 minutes until the solution had become distinctly alkaline. This occurred when the volume of the gas collected per minute decreased considerably. The solution, having become alkaline, absorbed more carbon dioxide and in place of some of the ethane, methyl alcohol was formed and remained in solution.

The solution before electrolysis had a p_H of 6.4 and after electrolysis a p_H of 10.

From the percentages of ethane, hydrogen, oxygen and carbon dioxide were subtracted the percentages of these gases arising from the Kolbe and Faraday reactions. This left carbon dioxide and hydrogen from other processes. This residual gas together with the percentage composition is given by the following table:-

Table 16. /

Table 16.

Time in minutes	15	30	45	60	75
CO_2	48.4	48.0	47.3	46.0	23.3
O_2	0.4	0.45	0.5	0.8	1.8
C_2H_6	22.6	22.5	21.7	20.9	23.1
H_2	28.6	29.1	30.5	32.3	51.8
Residual CO_2	3.2	3.0	3.9	4.2	--
$\frac{1}{2}$ Residual H_2	2.6	2.9	3.9	4.9	--

As the equations (d), (e) and (f) on page 2 show, residual CO_2 = $\frac{1}{2}$ residual H_2 for complete oxidation, and for partial oxidation to methyl alcohol or to ester residual CO_2 = residual H_2.

In the first two samples the residual CO_2 is greater than the half of the residual H_2. The presence of ester is indicated since the solution is still acid, although most of the oxidation current gives complete oxidation.

The analysis of the third sample suggests that three reactions only are taking place, Kolbe, Faraday and complete oxidation.

The next sample was evidently taken when the solution had becom alkaline for the residual CO_2 is less than half the residual H_2. As the total CO_2 in the final sample was less than the amount corresponding to the /

the ethane formed, the solution must have become decidedly alkaline.

Oxidation Current at Higher Temperatures.

Some of the same solution was electrolysed at 70°C with the same current density. Samples of the gas were taken after a preliminary run of 3/4 hour. From the analysis of the gas were calculated the residual percentages of CO_2 and H_2 :-

Composition of gas:-

C_2H_6	10.6
H_2	48.9
O_2	5.8
CO_2	34.7

$C_2H_6 / H_2 = 21.7$

Residual CO_2 = 13.5

$\frac{1}{2}$ Residual H_2 = 13.35

The residual CO_2 is approximately equal to half the residual H_2. Thus at 70°C the main reactions are Kolbe, Faraday and complete oxidation.

The experiment was repeated at 95°C, the other conditions being kept the same.

Composition of gas:-

C_2H_6	1.8
H_2	65.0
O_2	22.8
$C\Theta_2$	10.4

$C_2H_6 / H_2 = 2.77$

Residual CO_2 = 6.8

$\frac{1}{2}$ Residual H_2 = 8.8

The /

The residual CO_2 is actually less than half the residual H_2 and no process can account for this. Carbon monoxide was tested for but found absent. The only other explanation was the frothing which took place during electrolysis at this temperature. Solution was carried over with the gases and on cooling to room temperature dissolved some of the carbon dioxide . The results, however, are approximate enough to show that most of the oxidation current is given to complete oxidation.

Methane.

If two gases are exploded with excess of oxygen, it is an easy matter to estimate the percentage composition of the mixture. This is not possible if three combustible gases are present. In the above experiments it was assumed that the gases exploded were ethane and hydrogen, methane being absent. If all three are present hydrogen may be absorbed by palladium, but since hydrogen is the main constituent the method is hardly practicable. The other way is to collect the anode and cathode gases separately, with the assumption that hydrogen is not present in the anode gas.

For this purpose a porous pot, 9 cms. long with an internal diameter of 2 cms., was fitted with a rubber /

rubber stopper through which passed a platinum spiral, which served as the anode, and an outlet tube. The anode was made from 20 cms. of wire, 0.86 m.m. in diameter, and the cathode of similar wire was wound round the pot. The latter was placed in a wide-mouthed test tube and held in position by an ordinary stopper. As only methane was being tested for, the cathode gases were allowed to escape into the atmosphere.

The electrolyte was composed as follows:- 250 c.c. of the solution contained 25 gms. of potassium acetate and 25 gms. of acetic acid. Part of the solution was electrolysed and the gases evolved led into the remainder to saturate it. The cell was then almost filled with solution, placed in the thermostat at 70°C and allowed to reach that temperature. To minimise the resistance due to the porous pot suction was applied to the outlet tube and solution drawn into the pores.

A voltage of 7 volts across the electrodes gave a current density of 0.5 amp. / cm^2

The solution in the anodic chamber always remained acid but from time to time acetic acid was added to the cathodic liquid. Half an hour was allowed for the gases within the pot to reach equilibrium before samples were collected over mercury and analysed. Oxygen was present in trace and carbon dioxide was not measured.

If /

If the equations for the complete combustion of ethane and methane are examined it is found, in the case of ethane,

$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O ,$$

that the contraction in volume on explosion (C) = 5 volumes and on absorbing the carbon dioxide with potash that the volume absorbed (A) = 4 volumes so that the ratio C/A = 5/4 = 1.25, and in the case of methane,

$$CH_4 + 2O_2 = CO_2 + 2H_2O ,$$

that C/A = 2.0.

If, in the above experiment, C/A = 1.25 the gas will be pure ethane. A ratio of 2 corresponds to pure methane while ratios between 1.25 and 2 represent mixtures of the two gases.

Analysis of the gases gave a value of C/A equal to 1.26. This corresponds to not more than 2% of methane at 70°C.

The experiment was repeated at a temperature of 95°C when the ratio was found to be 1.267. This value represented not more than 4½% of methane.

It is to be concluded that the main reactions taking place in the electrolysis of aqueous acetates at different temperatures are, the Kolbe reaction, the Faraday reaction and complete oxidation.

Influence of Current Density on the Ethane Yield.

Murray (5) studied the influence of current on the yield of ethane by varying the voltage between the electrodes /

electrodes i.e. by a change in the external resistance. The ethane yield increased rapidly at first with the current, until a maximum was obtained. Further increase in the current produced no variation in the yield. Murray also stated that the result was the same whether resistances were applied externally or internally. An experiment was performed to verify this. Small current densities were used, for it was thought that greater differences in the ethane yield, if any, would then be shown.

A 5% acetate solution, containing 4% of acetic acid, was electrolysed with current densities not greater than 0.25 amp. / $cm.^2$

With the type of cell used in the previous experiments the gases were evolved between the electrodes and the internal resistance varied considerably. To eliminate this effect a U-tube was employed as a cell. An electrode was placed in each limb and gases could rise without disturbing the solution between the anode and cathode.

The U-tube was 15 cms. in height and had limbs $1\frac{1}{4}$ cms. in diameter. The side tubes were lengthened, bent round towards each other and joined. An outlet tube was attached to this connecting tube and delivered the gas from both electrodes into a reservoir of mercury.

The electrodes, of fairly stout platinum wire, were bent into the form of flat spirals which just

fitted /

fitted the limbs of the tube. The latter was also provided with rubber stoppers which carried the spirals and by means of which the distance between the electrodes could be varied.

Solution was poured into the cell to within a short distance of the top to prevent a large air space when the stoppers were inserted. A current was now passed. Mixing of the solution could not take place to the same extent as it did in the other cell. Here the cathodic liquid would tend to become alkaline and concentration polarisation would set in.

A preliminary experiment was performed to find the most suitable time to collect the gas. A definite voltage was applied and the current reading taken every minute. At first the current rose fairly rapidly but became steady after five minutes. After about an hour it fell off again as a result of concentration polarisation. A different voltage was applied and a similar result obtained. In the actual experiment ten minutes was given to allow the gases to reach equilibrium, the solution still being acid.

The tube was rinsed out after each electrolysis and filled with a fresh portion of solution. In the first part of the experiment the electrodes were kept at a fixed distance apart and external resistances applied by means of changes in the voltage across the electrodes./

electrodes. In the second part the voltage across the electrodes was kept constant and the current density varied by moving the electrodes closer together or further apart. The following table gives the values for the ethane:hydrogen ratios:-

Table 17.

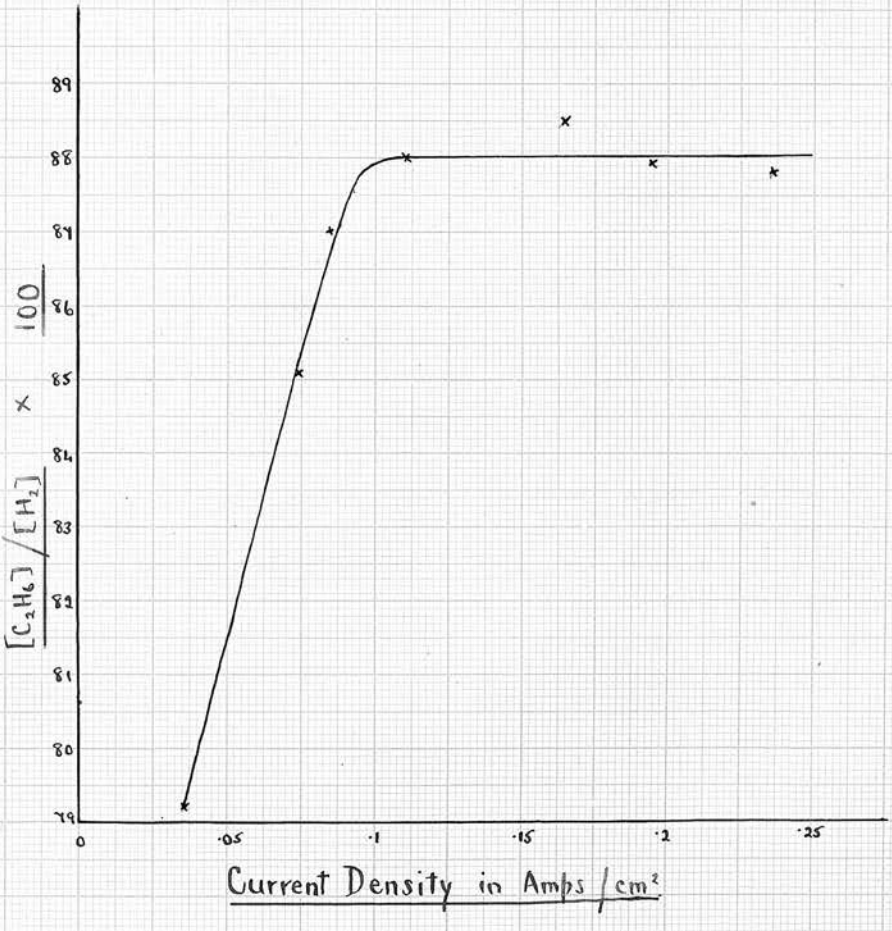
Voltage across Electrodes.	Current Density	100 x C_2H_6/H_2
54	0.237 amp./cm.^{2}	87.8
44	0.165	88.5
24	0.075	85.1
13	0.037	79.2
32	0.085 amp./cm.^{2}	87.0
32	0.110	88.0
32	0.195	87.9

The ratio of ethane to hydrogen was plotted against current density as in Fig.12.

The points from both experiments were found to lie on the same curve. This means that the current ethane yield is independent of the applied voltage, it depends only on the current density, i.e. the ethane yield is the same whether the current density is lowered by applying an internal or external resistance.

Nature /

Fig. 12.


89
88
87
86
85
84
83
82
81
80
79
0
·05
·1
·15
·2
·25
[C2H6] / [H2] × 100
Current Density in Amps / cm²

Nature of the Anode.

On account of the high current ethane yield which they give, bright and grey platinum have been most frequently used in the electrolysis of aqueous acetate solutions. Platinum and gold are the two extremes, no ethane being obtained with a gold anode under ordinary conditions. Between these stand iridium, carbon, platinised platinum and palladium. Of these palladium is most like gold for no ethane is given.

Preuner and Ludlam[12] observed no ethane with platinised platinum electrodes but complete oxidation. The amount of oxidation, however, according to Robertson[15] was greater than with gold electrodes. Carbon, giving a moderate ethane yield and complete oxidation, occupies a position between bright platinum and platinised platinum.

The influence of anode material with regard to potential was studied by Foerster and Piguet[16] and more recently by Gibson[14] who showed that a definite anode voltage was necessary for ethane synthesis.

A striking resemblance exists between the curves obtained (a) by the electrolysis at a platinum anode of aqueous acetates at different temperatures (Fig. 6) /

(Fig.6) and (b) by the electrolysis at a gold anode of an acetate solution in acetic acid with varying amounts of water added to the solvent (Fig.4).

In (a) the ethane yield diminished with rise in temperature of the solution, oxidation increased to a maximum and then fell off, while the free oxygen yield increased. In (b) there was a similar state of affairs. With the addition of water to the solvent, the ethane yield diminished, oxidation increased to a maximum and fell away, while the oxygen yield increased. There appears to be some relationship between temperature, the nature of the anode and of the solvent. This can be made more apparent by a few additional experiments.

It has already been shown, by increasing the concentration of the solution, that higher ethane yields are obtained at higher temperatures and that the maximum in the oxidation curve is displaced to higher temperatures. It might be expected, then, with the electrolysis at a gold anode of aqueous acetates, that increase in the concentration of the solution will be accompanied, if not by the formation of some ethane, at least by increased oxidation.

In the following experiments electrolysis of aqueous acetates was conducted at different anodes with variations in the concentration.

Gold Anode.

When /

When a dilute aqueous acetate solution is electrolysed at a gold anode the gold disintegrates and the gases formed are mainly oxygen and hydrogen. Most of the current is therefore given to the Faraday reaction.

Electrolysis of Concentrated Aqueous Acetate Solutions.

100 c.c. of solution contained 35 gms. of potassium acetate and 6.5 gms. of acetic acid.

Current Density = 0.5 amp/cm^2.

The current was passed for 25 minutes before the gas was collected. Disintegration of the anode took place.

Composition of the gas:-

O_2	25.2
C_2H_6	1.25
H_2	73.5

Distribution of current:-

Kolbe	1.7
Oxidation	29.8
Faraday	68.5

A small amount of ethane has been formed. The results are not very convincing but are sufficient to indicate that oxidation is greater than with more dilute solutions.

Platinised Platinum Anode.

Oxidation Current.

Preuner /

Preuner and Ludlam (loc.cit.) assumed from the presence of carbon dioxide among the gases that complete oxidation took place at platinised platinum electrodes. This was first of all verified and an estimation made of the oxidation current.

Carefully cleaned platinum electrodes were platinised in a solution of platinic chloride with a small current which was reversed every minute. When a thick velvet layer had appeared on the surface the electrodes were carefully washed and electrolysed in an acetate solution to remove chlorine.

A 10% acidified solution of acetate in water was saturated with carbon dioxide and electrolysed. Current Density = 0.5 amp /cm^2. The gas was collected when the electrolysis had proceeded for 3/4 hour, the solution still being acid. Residual carbon dioxide and hydrogen were calculated as before and compared.

Composition of the gas:-

O_2	9.2
C_2H_6	4.6
H_2	59.5
CO_2	26.7

Residual CO_2 = 17.5

$\frac{1}{2}$ Residual H_2 = 18.2

The residual current is evidently used up in complete oxidation.

The /

The distribution of current is as follows:-

Kolbe	7.7
Oxidation	30.9
Faraday	61.4

Electrolysis of a Concentrated Aqueous Solution.

100 c.c. of this solution contained 35 gms. of potassium acetate and 6.5 gms. of acetic acid.

Current Density = 0.5 amp. /cm^2.

The electrolysis of the above solution was allowed to proceed for half an hour before the gas was collected and analysed. The composition of the gas was as follows:-

O_2	1.2
C_2H_6	34.23
H_2	64.57

Distribution of current:-

Kolbe	53.0
Oxidation	43.3
Faraday	3.7

It will be observed from a comparison of the products given by dilute and concentrated solutions, that when the concentration of the solution is increased the ethane yield is considerably increased and less free oxygen appears.

Carbon /

Carbon Electrodes.

Electrolysis of a 10% aqueous acetate solution at carbon electrodes with a current density of 0.5 amp. per $cm.^2$ gave no oxygen but an ethane:hydrogen ratio of 20.8. Oxidation took place to the extent of 79.8%. A 35% acetate solution gave with the same current density a 39.6% yield of ethane and 60.4% oxidation. Thus the ethane yield has been doubled at the expense of the oxidation current.

Discussion.

The nature of the anode appears to have less effect the more concentrated the solution. Increase in the concentration, on the basis of catalytic action, is equivalent to removal of part of the water around the anode. The effect, however, is not so great as that produced by the replacement of the solvent by a non aqueous one, i.e. by the complete removal of the water, when high ethane yields are always obtained.

It would appear from above that different anodes have different adsorption powers. Thus it could be argued that gold adsorbs more water than platinised platinum and platinised platinum more than bright platinum. The whole problem is too complicated, however, to proceed much further in the meantime.

-----oOo-----

Electrolysis of Acetate Solutions in Presence of Borax.

(1) A 20% acetate solution containing 1% of borax was electrolysed with a current density of 0.5 amp/cm^2 for half an hour and samples of the gas analysed . The solution which was slightly alkaline at the beginning had turned decidedly alkaline.

No oxygen was found but methyl alcohol was detected. The ratio of ethane to hydrogen gave a value of 0.55.

Borax appears to act in the same way as bicarbonate and carbonate in the Hofer and Moest reaction. The ethane yield is considerably higher here but if attention were paid to the concentration, etc., a better alcohol yield might be given.

(2) A 10% acetate solution containing 5% of borax was acidified with acetic acid and electrolysed with the same current density as above. The analysis of the gases showed 0.44% of oxygen to be present and the ethane:hydrogen ratio to be 0.853.

Borax has little effect on the electrolysis of aqueous acetates beyond the effect of acid or alkali.

-------oOo-------

Quantitative Determination of the Hofer and Moest Process.

Hofer and Moest (2) obtained good yields of methyl alcohol by electrolysing aqueous acetate solutions in the presence of carbonate and bicarbonate, the net process being as follows:-

$CH_3COO + OH = CH_3OH + CO_2$ at the anode

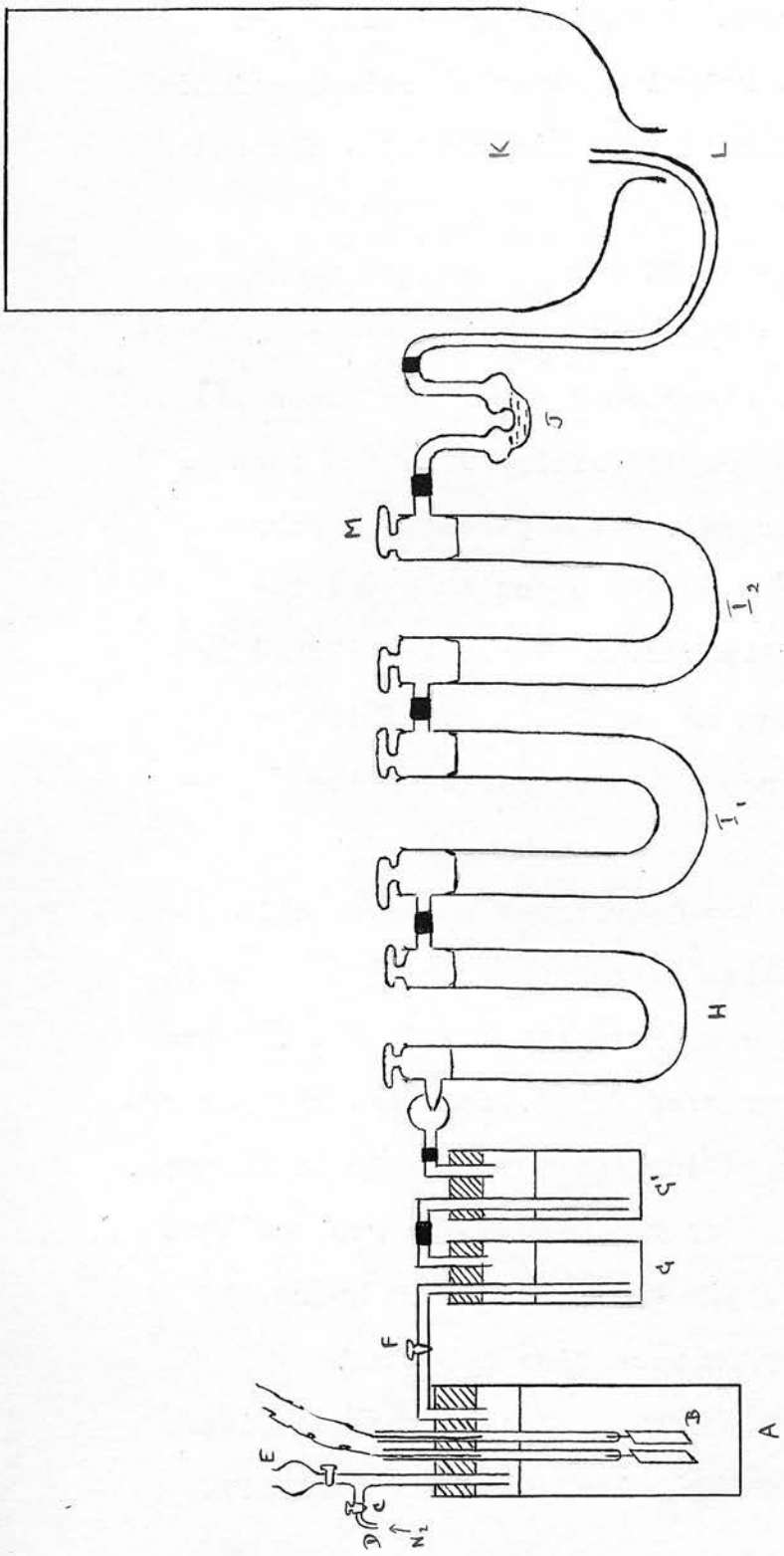
and $H + H = H_2$ at the cathode.

Ethane and oxygen were also found among the gases and small amounts of formaldehyde arising from the further oxidation of methyl alcohol. The percentage current used for oxidation purposes was calculated and the assumption made that this current was all utilised in methyl alcohol formation or partly in formaldehyde formation. No allowance was made for complete oxidation.

The investigators performed a large scale experiment with a solution containing the most suitable quantities of acetate, carbonate and bicarbonate. The platinum anode had an area of 50 sq. cms. and the cathode 20 sq. cms. The average current was from 10 to 20 amps. Acetic acid was added every ten minutes to replace that used up in the electrolysis which lasted 20 hours. Carbon monoxide and oxygen were also detected.

Estimating aldehyde as alcohol they obtained a total of 86 gms. of methyl alcohol, whereas if all

Fig. 13.



the current had given methyl alcohol they would have obtained 119.6 gms. They finally ascertained that if oxidation current went to the formation of methyl alcohol they had a 93% yield. The other 7% had been lost in the process. Now although methyl alcohol is rather difficult to estimate quantitatively, it is possible that part of the current gives complete oxidation. To test this, an estimation had to be made of the carbon dioxide formed during the electrolysis.

Experimental.

The cell A, Fig,13, was fitted with a rubber stopper bored with four holes through which passed the two electrodes, an inlet and an outlet tube. The platinum electrodes B had each an area of 2sq.cms. and were fixed about 1 cm. apart. The inlet tube C could either be exposed to the air through a tap D or connected to a funnel E. The outlet tube F passed into a wash-bottle G which was connected in a similar way to a wash-bottle G'. Both bottles contained distilled water.

Gases bubbling through the bottles were dried by the calcium chloride tube H and passed through the weighed soda-lime tubes I_1 and I_2 where the carbon dioxide was removed. The gases finally passed through a bubbler J and were collected over water in the winchester K.

Solution /

Solution.

500 c.c. of solution contained:-

100 gms. of potassium acetate
21 gms. of .. carbonate
17 gms. of .. bicarbonate

The carbon dioxide was boiled off from this solution.

Procedure.

25 c.c. of the solution was placed in the cell A. A nitrogen cylinder was attached to the tap D and a slow current of gas passed through the apparatus until the gas collected at L had the same composition as that entering at D. It was then assumed that all air had been driven out. The taps were then closed and the soda-lime tubes weighed and refitted to the apparatus. To make sure that the latter was air-tight a syphon arrangement was attached to L and gentle suction applied. Water ceased to run out of the syphon after a few minutes. Nitrogen was again passed through to establish equilibrium. L was replaced below the inverted winchester filled with water.

The cell was placed in the thermostat at 25°C and a current of 1 amp. passed . Methyl alcohol was trapped by the wash-bottles, carbon dioxide by the soda-lime while ethane, hydrogen, oxygen and nitrogen bubbled into the winchester. As heat was evolved in the soda-lime tubes where absorption was taking place

a /

a rough estimate could be made of the amount of soda-lime used up at any particular time.

Acetic acid was added every quarter of an hour to replace that lost in electrolysis. When electrolysis had been conducted for $4\frac{1}{2}$ hours the current was stopped and nitrogen again passed through slowly to drive the residual gas into the winchester. The same time was given to this procedure as in the preliminary removal of air from the apparatus and the same pressure of nitrogen was applied.

The gases in the winchester were analysed in the usual way. Samples were taken for analysis and the total volume of gas estimated at N.T.P. Oxygen was absorbed by pyrogallol, ethane and hydrogen were flashed with excess of oxygen and the residual gas was assumed to be nitrogen. The cylinder nitrogen contained oxygen as impurity and a small correction was made.

Increase in the weight of the soda-lime tubes gave the weight of carbon dioxide which had passed over from the cell and wash-bottles.

The solution from A, G and G'was washed into a standard flask and made up to the 100 c.c. mark with distilled water. The carbonate was estimated in a portion of this solution and the total carbonate in the final solution calculated as CO_2. To this was added the weight of CO_2 collected in the soda-lime tubes /

tubes and the total CO_2 after electrolysis ascertained. The total CO_2 before electrolysis was found from the analysis of the original solution. By subtraction, the amount of CO_2 formed in the actual electrolysis was determined.

As far as the carbon dioxide was concerned, it did not matter how much acetic acid was added during the electrolysis. If excess of acetic were added there would have been less CO_2 in A and more in the soda-lime tubes, or if insufficient acid were added then, owing to the greater alkalinity of the solution, more CO_2 would have been retained in A. It was not essential to estimate the acetate but since the composition of the solution at the beginning, according to Hofer and Moest, gave the best alcohol yield, it was advisable to keep the proportions as constant as possible throughout.

The methyl alcohol was distilled off from the remainder of the solution and from its density the weight of methyl alcohol formed in the electrolysis was determined.

The formaldehyde was neglected as a preliminary investigation indicated a yield even less than that of Hofer and Moest.

Preliminaries. Methyl Alcohol Estimation.

A /

A solution containing a known weight of methyl alcohol was made up. 6.55 c.c. of methyl alcohol was placed in a flask with potassium acetate, bicarbonate and carbonate, in roughly the proportions in which they occur in the above solution, and diluted with water to about 100 c.c. The methyl alcohol was found by pycnometer and hydrometer methods to have a density of 0.794. Hence the weight of alcohol taken was 5.16 gm.

The above solution was distilled in a flask fitted with a fairly short spiral fractionating column. Distillation began at 65°C but the temperature rose almost immediately to over 90°C. The first 5 c.c. of the distillate contained 58% by weight of alcohol, the succeeding 5 c.c.'s, 27%, 26%, 4%, 2%, 1%, respectively, so that most of the alcohol had distilled over when 30 to 35 c.c. of the distillate had collected.

The total distillate amounted to 36 c.c. Its density by the pycnometer method was 0.978 and by the hydrometer method 0.977 to 0.978. The total alcohol recovered was 4.68 gms. The percentage of alcohol recovered was 90.7%, which factor was applied in the determination of alcohol in the electrolysis.

Carbonate Estimation.

0.7 gm. of dry potassium carbonate was

washed into a 400 c.c. beaker and the solution diluted to about 200 c.c. with water. To the boiling solution was added drop by drop a moderate excess of boiling calcium chloride solution. Boiling was continued for five minutes to convert any bicarbonate into carbonate. The precipitate was allowed to settle when a few more drops of the calcium chloride solution were added to ensure complete precipitation. If no further precipitation took place the precipitate was again allowed to settle and left for an hour.

The liquid above the precipitate was decanted through a weighed Gooch crucible. The precipitate was washed twice by decantation with freshly distilled water containing ½% of calcium chloride, the liquid being poured into the Gooch. The calcium carbonate was then transferred to the crucible and washed with 40% and finally with 90% alcohol. The Gooch was left in an oven at 100°C for an hour and after cooling was weighed. The following are the results:-

Weight of glass + K_2CO_3 = 6.0858 gms.
.. .. .. = 5.3918 ..
Weight of K_2CO_3 = 0.6940 ..
= 0.5029 gm. $CaCO_3$.

Weight of Gooch + $CaCO_3$ = 15.3215 gms.
.. .. .. = 14.8308 ..
Weight of $CaCO_3$ = 0.4907 gm.

Percentage of CO_3" recovered = 97.6%

The experiment was repeated with about 0.5gm. of dry potassium bicarbonate.

Results:- /

Results:-

Weight of glass + $KHCO_3$ = 5.9360 gms.
.. .. .. = 5.3916 ..
Weight of $KHCO_3$ = 0.5444 ..
= 0.5444 gm. $CaCO_3$

Weight of Gooch + $CaCO_3$ = 13.3491 gms.
.. .. .. = 12.8167 ..
Weight of $CaCO_3$ = 0.5324 gm.

Percentage of CO_3" recovered = 97.8%

The mean factor 97.7% was applied to the actual carbonate estimation.

In the above analysis care had to be taken in the washing of the precipitate since the addition of carbon dioxide would form the soluble bicarbonate. Water was driven from the wash-bottles by means of a current of air, obtained from a water pump and dried by calcium chloride and soda-lime.

Analysis of Solutions.

Carbonate in Original Solution.

10 c.c. of the original solution was treated as above for carbonate. The following are the results of two estimations:-

		I	II
Weight of Gooch + $CaCO_3$	=	15.2990 gms.	13.4073 gms.
.. .. ..	=	14.7061 ..	12.8167 ..
Weight of $CaCO_3$	=	0.5929 gm.	0.5906 gm.

Mean weight of $CaCO_3$ = 0.5918 gm.

∴ 25 c.c. of solution equivalent to 1.4795gms.

Total CO_2 in original solution (correction made)
= 0.667 gm. CO_2

Carbonate /

Carbonate in Final Solution.

The contents of the cell and wash-bottles were transferred to a 100 c.c. flask and made up to the mark with water. 20 c.c. was then taken for analysis. It was found with the necessary correction made that the total carbonate in solution after electrolysis was equivalent to 0.5274 gm. of CO_2.

It will be observed on comparing this with the total carbonate before electrolysis that more acetic acid has been added to the solution than was used up in the electrolysis.

Soda-lime Tubes.

The following are the weights of the soda-lime tubes before and after electrolysis:-

Weight of tube(1) + CO_2 = 116.983 gms.
.. .. .. = 113.203 ..
Weight of CO_2 = 3.780 gm.

Weight of tube(2) + CO_2 = 105.494 gms.
.. .. .. = 105.485 ..
Weight of CO_2 = 0.009 gm.

Total CO_2 in tubes = 3.789 gms.

CO_2 at end of experiment = 3.789 + 0.5274 gms.
= 4.3164 gms.

CO_2 at beginning = 0.6670 gms.

Hence CO_2 formed = 3.6494 gms.
= 1855 c.c. at N.T.P.

Methyl /

Methyl Alcohol Estimation.

80 c.c. of the solution from the cell and wash-bottles was distilled. The density of the distillate was then taken.

Weight of flask + CH_3OH = 55.230 gms.
.. .. .. = 28.609 ..
Weight of CH_3OH = 26.621 gms.

Density = 0.9945 at 15°C

Composition of Solution = 2.6 gms. CH_3OH per 100 gms solution.

Total weight of methyl alcohol (correction applied) = 0.954 grams.

Gas Analysis.

Nitrogen.

The percentage of oxygen in the nitrogen from the cylinder was estimated by absorbing it with pyrogallol.

100.52 volumes of cylinder gas contain 0.52 volumes of oxygen, i.e. 100 volumes of pure nitrogen have 0.52 volumes of oxygen mixed with it.

1st. Winchester.

Volume of gas for analysis = 45 c.c.
Gas left in winchester = 2432 c.c.
Total gas = 2477 c.c.
Temperature =11°C
Barometer = 743.6 m.m.
Vapour Pressure = 9.8 m.m.

Volume of gas in winchester at N.T.P. = 2300c.c.

The /

The following table gives the percentage composition of the gases and the volume of each gas present:-

Table 18.

Gas.	1st Sample	2nd Sample	Mean Value	Volume in cc. at N.T.P.
O_2	4.27	4.45	4.36	100.3
C_2H_6	11.64	11.59	11. 61	267.0
H_2	57.45	57.21	57.33	1318.6
N_2	26.64	26.75	26.7	614.0

2nd. Winchester.

Total volume of gas = 716 c.c. at N.T.P.

Table 19.

Gas.	1st Sample	2nd Sample	Mean Value	Volume in cc. at N.T.P.
O_2	1.43	1.32	1.37	9.8
C_2H_6	10.86	10.90	10.88	77.9
H_2	68.70	68.78	68.74	492.3
N_2	19.01	19.0	19.0	136.0

The corresponding volumes in the first and second winchesters were added together. A small amount of oxygen was subtracted (impurity in the N_2). The following are then the results:-

O_2 106 c.c.
C_2H_6 345 c.c.
H_2 1811 c.c.

CO_2 1855 c.c.
CH_3OH 0.954 gm.

The /

The whole experiment was repeated with 30 c.c. of solution in the cell. As the results turned out approximate to those above a summary only will be given:-

O_2	103c.c.	CO_2	1512 c.c.
C_2H_6	247.5 c.c.	CH_3OH	1.008 gms.
H_2	1932.0 c.c.		

The corresponding amounts from both experiments were added together to give the following totals:-

O_2	209.0 c.c.
C_2H_6	592.5 c.c.
H_2	3743.0 c.c.
CO_2	2367.0 c.c.
CH_3OH	1.962 gm.

The volumes of gases arising from the Kolbe, the Faraday and the Hofer and Moest reactions are then subtracted from the total gases. The residual gases are then CO_2 and H_2 whose volumes are compared. This is illustrated in the following table:-

Table 20. /

Table 20.

	C_2H_6	H_2	O_2	CO_2	CH_3OH
Totals	592.5cc	3743cc.	209cc.	3367cc	1.962gm
Kolbe	592.5	592.5		1185	
Faraday		418	209		
Hofer-Moest		1373		1373	1.962gm
Total Product accountedfor	592.5	2384	209	2558	1.962gm
Residual Gas		1359		809	

Residual CO_2 = 809 c.c.
$\frac{1}{2}$Residual H_2 = 680 c.c.

For complete oxidation half the residual hydrogen is equal to the residual carbon dioxide. These amounts compare favourably and show that complete oxidation does take place.

If it is assumed that all the residual hydrogen is formed through complete oxidation the distribution of current in the various processes is as follows:-

Hofer and Moest	36.7%
Kolbe	15.8%
Faraday	11.2%
Complete oxidation	36.3%

The fact that the residual carbon dioxide is in excess of half the residual hydrogen suggests that /

that all the methyl alcohol has not been obtained, even after a correction has been made. The residual CO_2 and H_2 may be divided up as follows to give exactly complete oxidation and methyl alcohol:-

	CO_2	H_2
A Methyl Alcohol	260 c.c.	260 c.c. + CH_3OH(lost)
B Complete Oxidation	549c.c.	1099 (2 x 549.5) c.c.
Totals	809 c.c.	1359 c.c.

The distribution of current is then as follows:-

Hofer and Moest	43.6%
Kolbe	15.8%
Faraday	11.2%
Complete Oxidation.	29.4%

This seems a more reasonable distribution of current. The alcohol yield is only half that obtained by Hofer and Moest although the conditions were made as nearly the same as possible. Methyl alcohol is very difficult to estimate but the carbon dioxide estimation given above was fairly accurate. For a greater alcohol yield than 43.6% a much greater volume of CO_2 would require to have been obtained, far beyond the limits of experimental error. It is apparent, then, that complete oxidation takes up a fair amount of the current.

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SUMMARY.

1. Electrolysis of acetate solutions has been conducted under different conditions.

2. Electrolysis in non aqueous solvents gives products which vary little with temperature and anode material. With water present in the solvent products depend on temperature and on anode material.

3. In the electrolysis of aqueous solutions at platinum electrodes the current is distributed in three main reactions, Kolbe, Faraday and complete oxidation. At low temperatures ethane is the main product. The yield falls off with rise in temperature and complete oxidation increases to a maximum. Free oxygen now appears. With a further rise in temperature the ethane yield becomes practically zero, complete oxidation decreases and the free oxygen yield increases.

4. An explanation of the course of the reaction is suggested on the basis of the discharged ion theory. The peroxide theory is possible but the oxidation theory does not explain the results.

5. Higher ethane yields are obtained at higher temperatures by the electrolysis of more concentrated solutions /

Summary (contd.)

solutions. Increase in the current density also brings about increased yields. This is explained by the assumption that the anode behaves as a catalyst.

6. The different products derived from electrolysis of aqueous solutions at different anodes can also be explained on the above assumption.

7. A quantitative estimation of the Hofer and Moest methyl alcohol experiment has been made. The main reaction is the formation of methyl alcohol. Other reactions are ethane and oxygen formation. Residual current amounting to about 30% is used in complete oxidation.

In conclusion the author wishes to express his very grateful thanks to Sir James Walker for his encouragement and advice throughout the research. The author's thanks are due also to The Carnegie Trust for the Universities of Scotland for financial assistance, which enabled him to carry out the work.

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